A Study of the Effects of Post-Combustion Ammonia Injection on Fly Ash Quality: Characterization of Ammonia Release from Concrete and Mortars Containing Fly Ash as a Pozzolanic Admixture

Final Report

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ABSTRACT

The Clean Air Act Amendments of 1990 require large reductions in emissions of NOx from coal-fired electric utility boilers. This will necessitate the use of ammonia injection, such as in selective catalytic reduction (SCR), in many power plants, resulting in the deposition of ammonia on the fly ash. The presence of ammonia could create a major barrier to fly ash utilization in concrete because of odor concerns. Although there have been limited studies of ammonia emission from concrete, little is known about the quantity of ammonia emitted during mixing and curing, and the kinetics of ammonia release. This is manifested as widely varying opinions within the concrete and ash marketing industry regarding the maximum acceptable levels of ammonia in fly ash. Therefore, practical guidelines for using ammoniated fly ash are needed in advance of the installation of many more SCR systems. The goal of this project was to develop practical guidelines for the handling and utilization of ammoniated fly ash in concrete, in order to prevent a decrease in the use of fly ash for this application. The objective was to determine the amount of ammonia that is released, over the short- and long-term, from concrete that contains ammoniated fly ash.

The technical approach in this project was to measure the release of ammonia from mortar and concrete during mixing, placement, and curing. Work initially focused on laboratory mortar experiments to develop fundamental data on ammonia diffusion characteristics. Larger-scale laboratory experiments were then conducted to study the emission of ammonia from concrete containing ammoniated fly ash. The final phase comprised monitoring ammonia emissions from large concrete slabs. The data indicated that, on average, 15% of the initial ammonia was lost from concrete during 40 minutes of mixing, depending on the mix proportions and batch size. Long-term experiments indicated that ammonia diffusion from concrete was relatively slow, with greater than 50% of the initial ammonia content remaining in an 11cm thick concrete slab after 1 month. When placing concrete in an enclosed space, with negligible ventilation, it is recommended that the ammonia concentration in the concrete mix water should not exceed 110 mg NH_3/L, if the NIOSH exposure limit of 25 ppm in the air is not to be exceeded. If even a modicum of ventilation is present, then the ammonia concentration in the concrete water should be less than 170 mg/L. The maximum level of ammonia in the fly ash can then be calculated using these limits if the concrete mix proportions are known.

In general, during the mixing and placement of ammonia-laden concrete, no safety concerns were encountered. The only location where the ammonia concentration attained high levels (i.e. > 25 ppm in the air) was within the concrete mixing drum.

EXECUTIVE SUMMARY

This project studied the release or emission of ammonia from mortar and concrete, and was undertaken because of the current and planned installation of selective catalytic and non-catalytic reduction (SCR and SNCR) systems at U.S. coal-fired power plants. It is known from U.S. and European experience that these ammonia injection technologies result in ammonia contamination of the fly ash, and that the use of this fly ash in mortar and concrete is associated with nuisance odors. The occurrence of ammonia odors, both during placement-finishing and curing, could cause the fly ash to be rejected for use as an admixture. Therefore, the main objectives of this study were 1) to gain an understanding of the behavior of ammoniated fly ash in mortar and concrete, 2) to develop practical guidelines for the use of ammoniated ash (i.e. how much ammonia is too much?), and 3) to transfer the results and recommendations to industry. It is hoped that this study will result in the continued use of fly ash in the wake of the wide-spread installation of SCR and SNCR systems.

The project was divided into three phases. The first phase focused on laboratory mortar experiments to develop fundamental data on ammonia release characteristics and to devise appropriate ammonia measurement techniques. Concrete experiments were then designed to study the emission of ammonia during mixing, placement and finishing, and curing. The final phase comprised monitoring ammonia release from large concrete slabs and comparing the data with those from the laboratory.

The results for mortar indicated that the overall ammonia loss rate was greater for mortar prepared at a higher water:cement+fly ash (W:CM) ratio, although the difference occurred mainly during the first 24 hours after placement. After 24 hours, the ammonia loss rates were similar. It is thought that this was caused by a greater amount of bleed water coming to the surface of the High W:CM mortar. Furthermore, the High W:CM mortar had a greater incipient porosity and thus diffusivity. At the end of 1 month, greater than 80% of the ammonia remained within the mortars. These data indicated that ammonia could continue to evolve from the mortar for a prolonged period after placement, although the rate would be very slow. It was also found that ventilation rate increased the ammonia loss rate from mortar, which suggested that a well-ventilated space could substantially increase the loss of ammonia from mortar and, by inference, concrete. The source of fly ash had a negligible influence on the long-term ammonia loss rate, when low-calcium Class F fly ash was used. However, mortar prepared using a higher-calcium fly ash evolved ammonia at a slightly slower rate than the Class F ash mortars. This was probably related to the faster rate of strength development that occurs when high-calcium fly ash is used in mortar, compared to Class F ash.

The concrete testing began with experiments designed to study the loss of ammonia during mixing. It was found that the size of the concrete batch exerted a pronounced effect on the ammonia loss rate during mixing. For a 20 L batch, the mixer was approximately ½ full whereas a 40 L batch was near the mixer capacity. After 40 minutes of mixing a 20 L batch contained substantially less of the initial NH_3 content than a 40 L batch. The implication of these data is that a full Ready Mix truck will retain

a larger proportion of ammonia than if the truck is not filled to capacity. In addition to batch size, the concrete mix proportions also affected the ammonia loss rate. In this case, a lower W:CM concrete lost less of its ammonia during mixing than a higher W:CM concrete. On average, it was found that approximately 85% of the initial ammonia content remained within the concrete after 40 minutes mixing.

One of the major concerns regarding the use of ammoniated fly ash in concrete is the potential exposure of workers to high levels of ammonia. A key issue is the maximum concentration of ammonia allowable in fly ash, below which worker safety would not be an issue. To address this concern, ammonia concentration in the air above fresh concrete placed in an enclosed space was measured over the course of 1 - 2 days. Ventilation rate and ammonia concentration were variables, and both ammoniated and non-ammoniated (with ammonia added to the water) fly ash were used. There was a clear positive relationship between ammonia concentration in the concrete and that in the air, with ventilation rate also having a substantial effect. From these data, the concentration of ammonia in fly ash that should not be exceeded in order to ensure worker safety was estimated. The data indicated that for concrete placed in areas with little to no air ventilation the ammonia concentration in the concrete water should not exceed 110 mg/L if the NIOSH recommended exposure limit TWA of 25 ppm is not to be exceeded. In areas with at least a modicum of ventilation, the maximum concentration in the concrete water would be about 170 mg/L. The maximum amount of ammonia in the fly ash will vary based on the concrete mix proportions and the fly ash content. The pertinent equation is then:

$$NH_{3water} = \frac{(NH_{3ash} \times FA)}{WF}$$

Where NH_{3water} is in mg/L, NH_{3ash} is in mg/kg, FA = unit fly ash content, and WF = unit water content.

As an example of the use of this equation, the maximum concentration of ammonia in fly ash is calculated here for a "typical" concrete with 326 kg/m^3 (550 lb/yd^3) of cementitious material, a W:CM ratio of 0.50, and a 20% fly ash replacement rate. It follows that for this mix, the ammonia concentration in the ash should not exceed 275 mg NH$_3$/kg for applications with negligible ventilation, and 425 mg/kg for applications with some degree of ventilation. If a greater proportion of fly ash is used then the ammonia concentration in the ash will need to be lower. Although a TWA of 25 ppm NH$_3$ in the air is considered safe, it would nonetheless produce a very strong, objectionable odor. Thus, in practice, a lower ammonia-in-air concentration is likely to be followed in order to minimize worker complaints. Assuming a more comfortable threshold of 10 ppm ammonia in the air, the maximum concentration in the concrete water would be approximately 50 and 75 mg NH$_3$/L for non-ventilated and ventilated conditions, respectively. Using the equation above, the estimated maximum ammonia concentration in the fly ash would then be 100 and 150 mg NH$_3$/kg ash for the two ventilation conditions.

The long-term loss of ammonia from concrete was studied over 1 month, with several variables tested. Unlike mortar, the concrete mix proportioning had no significant effect on the long-term rate of ammonia loss from concrete, nor did the ventilation conditions. The source of ammoniated fly ash also did not exhibit a noticeable effect on the long-term loss rate, when the data are expressed as a fraction of the initial ammonia content in the concrete. The data indicated that in an enclosed space the rate of ammonia loss from concrete is limited by diffusion through the concrete and not by the gas phase concentration of ammonia above the concrete. Therefore, it is inferred that exposure of the concrete outdoors, with a high degree of ventilation, prior to enclosure within a structure would not necessarily result in an increased loss of the ammonia within the concrete compared to a slab placed indoors with a lower degree of ventilation.

In general, the ammonia loss data indicate that after 1 month the loss rate had slowed significantly, although a substantial proportion of ammonia remained in an 11cm (4.3 in) slab of concrete. Moreover, a greater percentage of ammonia would remain in a thicker slab. Combining the mixing loss and long-term ammonia loss data, approximately 50% of the initial ammonia content remained in the concrete after 1 month time, and continued to diffuse from the concrete over the course of many months. However, at this point the rate was extremely slow, thus making long-term odors negligible. In our experiments, the ammonia concentration in the air decreased to less than 1-2 ppm within several days, even when using fly ash with a high concentration of ammonia. The residual ammonia in concrete would therefore be unlikely to cause any noticeable long-term odor problems, particularly for properly ventilated spaces.

The final phase of the project focused on the behavior of ammonia in Ready Mix concrete, during mixing, placement and finishing, and curing. Three 10 ft. X 15 ft. slabs (10-13 cm thick) were placed inside of vinyl buildings, and the ammonia concentration in the air monitored. Overall, the "field" data corresponded to the laboratory data. The maximum concentration of ammonia in the air within the buildings during placement and finishing agreed well with laboratory data, as did the amounts of ammonia loss during mixing. Similar to the lab experiments, the ammonia levels in the buildings decreased to less than 2 ppm within several days. Thereafter, no odors could be detected. In general, during the mixing and placement of ammonia-laden concrete, no safety concerns were encountered even when a fly ash containing 280 mg NH_3/kg was used. The only location where the ammonia concentration attained high levels (i.e. > 25 ppm in the air) was within the concrete mixing drum.

INTRODUCTION

The Clean Air Act Amendments of 1990 require large reductions in emissions of NOx from coal-fired electric utility boilers. This will necessitate the use of ammonia injection, such as in selective catalytic and non-catalytic reduction (SCR and SNCR) systems at many U.S. coal-fired power plants. In these systems some of the process ammonia inevitably "slips" through un-reacted, which results in the deposition of ammonia on the fly ash. It is well known from U.S. and European experience that these ammonia injection technologies result in ammonia contamination of the fly ash, and that the use of this fly ash in mortar and concrete is associated with nuisance odors. The occurrence of an ammonia odors, both during placement-finishing and curing, could cause the fly ash to be rejected for use as an admixture. Although there have been limited studies of ammonia emission from concrete, little is known about the quantity of ammonia emitted during mixing and curing, and the kinetics of ammonia release. This is manifested as widely varying opinions within the concrete and ash marketing industry regarding the maximum acceptable levels of ammonia in fly ash. Therefore, practical guidelines for using ammoniated fly ash are needed in advance of the installation of many more SCR systems.

The study presented herein was designed to address the concerns associated with the use of ammoniated fly ash in mortar and concrete. The main objectives of this study were 1) to gain an understanding of the behavior of ammoniated fly ash in mortar and concrete, 2) to develop practical guidelines for the use of ammoniated ash (i.e. how much ammonia is too much?), and 3) to transfer the results and recommendations to industry. It is hoped that this study will result in the continued use of fly ash in the wake of the wide-spread installation of SCR and SNCR systems.

The project was divided into three phases. The first phase focused on laboratory mortar experiments to develop fundamental data on ammonia release characteristics and to devise appropriate ammonia measurement techniques. Larger-scale concrete experiments were then designed to study the emission of ammonia during mixing, placement and finishing, and curing. The final phase comprised monitoring ammonia release from large concrete slabs and comparing the data with those from the laboratory.

EXPERIMENTAL
A.   Materials Sampling and Testing
A.1.   Fly Ash
Samples of fly ash were acquired from six different power plants. Three of these samples were collected by CAER staff, whilst the remaining three were collected by plant staff and shipped to the CAER. Approximately three 208 L (55 gal.) drums of each ash were obtained, and were tightly sealed and stored in an enclosed facility. The fly ash sources were selected based on ash quality (e.g. fineness, carbon content) and ammonia content. The sources and general properties of the fly ashes are provided in Table 1, ASTM C 618 required data in Table 2, and chemical composition is provided in

Table 3. The data indicate that seven of the fly ashes were marketable for use in concrete as a pozzolanic admixture, whereas the "Y" ash contains an excessive amount of carbon and thus does not pass ASTM C 618 requirements (max. 6% LOI). However, the relatively high ammonia content of this ash was desirable for studying ammonia loss from mortar and concrete. The chemical composition of each ash is reflective of the feed coal: power plant "R" burns primarily subbituminous coal, thus the ash contains a relatively high content of alkali and alkaline-earth elements. In contrast, the "MC" and "C" fly ashes contain comparatively large amounts of iron, indicative of a high-sulfur (i.e. pyrite) northern Appalachian feed coal that is burned at these power plants.

The ammonia content of the ammoniated fly ash samples was measured by mixing 50 g of fly ash with 150 ml distilled water in a polyethylene bottle. The mixtures were shaken periodically for approximately 24 hours, whereupon the solution was filtered. The pH of the filtrate was adjusted to greater than 11.5, and the ammonia content measured using an Orion 95-12 NH_3 electrode. The quantity of water soluble ammonia present on the ash was then calculated.

A.2. Aggregates

ASTM graded standard sand was utilized in the mortar experiments, and thus was not characterized at the CAER. In contrast, the coarse and fine aggregates that were used in the concrete experiments were characterized in accordance with ASTM C 29, C 70, C 127, C128, C 136, C 566, and D 75. A summary of these data are presented in Table 4. Approximately 5 tons of the coarse aggregate (ASTM designation "57") and 3 tons of the fine aggregate were obtained and stored in an enclosed facility.

B.   Mortar Preparation and Strength Testing

Mortar samples were mixed in accordance with ASTM C 305, using a Hobart mixer. Two mixes were designed to represent a fairly wide range of water:cement+fly ash (W:CM) ratio. A "Low W:CM Mix" was proportioned to meet ASTM C 109 specifications for a standard mortar, whereas the "High W:CM Mix" comprised a similar cement + fly ash:sand ratio, but a higher proportion of water (Table 5). All mortars in this study were prepared using ordinary Portland cement (OPC), fly ash, distilled water, and ASTM standard sand. A third mix ("UCS Mix"; Table 5) was designed and utilized for the compressive strength testing of mortar.

Ammonia was added to mortars prepared with non-ammoniated fly ash by completely dissolving ammonium sulfate (($NH_4)_2SO_4$) in the mix water, at a specified concentration, before the water was mixed with the OPC and sand. Although it is generally believed that ammonia is present in fly ash as NH_4HSO_4 (bisulfate), analysis of fly ash and deposits found on flue gas equipment (e.g. air heaters) have found ammonium sulfate, bisulfate, and sulfite (e.g. Jordan and Casper, 1995; van der Brugghen et al., 1995). No additional ammonia was added to mortars containing ammoniated fly ash.

During mixing of the mortars the space between the mixing bowl top and the mixer head was enclosed using a flexible plastic bag that was sealed to the bowl and mixer

using a rubber band. This set-up was utilized to minimize ammonia loss during mixing.

After mixing, mortar samples were prepared for UCS testing by casting into cube molds (5.1 cm X 5.1 cm X 5.1 cm) in accordance with ASTM C 109. The only significant deviation from ASTM specifications was the use of plastic molds instead of metal. The mortar cubes were cured for 24 hrs in high humidity. After this initial set, the samples were transferred to a humidity- and temperature-controlled curing room. UCS data were acquired after 7 days and 28 days curing.

C.   Concrete Preparation
Concrete studied in this project was prepared using Quickcrete brand OPC, graded sand, limestone aggregate, fly ash, and tap water. Slump was adjusted to 15 cm (6 in.) using a mid-range water reducer, and air was entrained by addition of an air entraining admixture. Concrete batch volumes of 0.02 m^3 were formulated following ACI 211.1-91 guidelines (ACI, 2000). Three W:CM ratio mixes were designed and prepared in trial batches, and are presented in Table 6. Ammonia was introduced into the concrete in a manner similar to that described for the mortar testing. The components were mixed for approximately 3 minutes in a 99 L (3.5 ft^3) capacity mixer, the opening of which was covered with a tight-fitting lid to prevent the escape of ammonia from the rotating drum during mixing.

D.   Measurement of Ammonia Loss from Mortar and Concrete
D.1.   Effects of Ammonium Salt Type
The effect of salt type on ammonia loss from mortar was evaluated using the Low W:CM ratio mortar, prepared in 2 L batches as described above. Ammonia was added by dissolving ammonium chloride (NH_4Cl), ammonium sulfate (($NH_4)_2SO_4$), or ammonium bisulfate (NH_4HSO_4) in the mix water at a concentration of 122 mg NH_3/L. Immediately after mixing, the mortar was placed into a 15.2 cm (6 in.) diameter by 30.5 cm (12 in.) long plastic cylinder that contained 2.5 L of damp Ottawa sand at the base. The wet mortar was rodded 30 times, the surface smoothed with a rubber spatula, and the cylinder sealed using a plastic "snap" lid fitted with a corked two-hole rubber stopper. At specified intervals, the ammonia concentration in the 1 L head-space was measured using a Sensidyne ammonia detection tube. After each measurement, the plastic lid was removed to permit ammonia to be lost to the atmosphere. Prior to the next reading, the plastic lid was snapped back into place and the next ammonia measurement acquired ten minutes after the cylinder was sealed. This procedure was repeated over the course of approximately 20 hrs. Although the methodology did not produce a quantitative measure of the total ammonia lost from the mortars, it did provide a useful comparison between the different ammonium salts.

D.2.   Ammonia Loss from Mortar
Based on ammonia measurement technique testing described above, a modified experimental set-up was devised for the measurement of ammonia loss from mortar. For this procedure, two holes were pre-drilled into the sides of a cylinder, near the top

edge, and fitted with tight-fitting rubber grommets through which a flow of air was passed into and out of the cylinder head-space (Figure 1). Before entering the cylinder, the air was passed through a bed of carbon-impregnated-with-sulfuric acid (CISA) beads to remove any ammonia, then through a flask containing distilled water to humidify the air. The effluent (containing ammonia from the mortar) was passed through a diffuser that was placed into a 250 ml Erlenmeyer flask containing the magnesium acetate-acetic acid trap solution (Figure 1).

The trap solution was periodically sampled during the experiment, using a plastic syringe, and the ammonium concentration measured using an Orion ammonium ISE. Although the ammonium electrode in traditional use suffers interferences from other monovalent cations in solution, in this application the only cations present apart from ammonium (NH_4^+) are hydronium (H_3O^+) and magnesium (Mg^{2+}), which produce negligible interference at the 0.1 ionic strength and pH (4.74) of the trap solution. Furthermore, calibration of the ammonium electrode is accomplished using the same solution as the trap solution. Upon completion of the measurement, the sample solution was returned to the Erlenmeyer flask. Evaporation of the trap solution was compensated for by recording the initial weight of the flask + solution and adding fresh solution each day in sufficient quantity to return the flask to the initial weight.

Ventilation rates through the cylinders were chosen to represent a range of conditions that would be encountered indoors. The rationale for selection of ventilation rates was based on the requirements for outdoor air ventilation in a residential living area (ASHRAE 62-1999). The standard requires a ventilation rate of 15 ft^3/min/person (425 L/min/person) for an occupied living space. For example, a basement room size of 6 m X 6 m X 2.4 m has a volume of 87,840 L. If the ventilation rate is calculated for 5 persons, then the total rate is 2125 L/min. Our laboratory experimental design represents a cylindrical segment of the room that is 15.24 cm in diameter X 2.4 m high, with a volume above the slab of 41 L. It follows that the proportional air ventilation rate is 1.08 L/min. Therefore, a ventilation rate of 1 L/min was chosen as the "base rate" for our mortar experiments. However, the rate was varied from 0.5 to 15 L/min in order to investigate the influence of ventilation on ammonia loss rate.

It should be kept in mind that even the high ventilation rate of 15 L/min, where the air was being replaced every 4 seconds, represents a wind speed of only 0.067 miles/hr, which is significantly below wind speeds encountered outdoors even on a fairly calm day. In order to replicate outdoor exposure conditions a very high ventilation rate would be required while still capturing all of the evolved ammonia in our trap flask. For example, to simulate a 1 mile per hour wind speed in the 15 cm X 30 cm cylinder with a 5.5 cm tall head-space would require a ventilation rate of 225 L/min through the cylinder. At this rate, configuring the experiment to trap all of the evolved ammonia would be extremely difficult. Also, outdoor applications are not as much a concern for ammonia odors as are indoors applications. Therefore, the focus of our study was to simulate realistic indoor conditions.

One of the major concerns regarding the use of ammoniated fly ash in mortar and concrete is the potential exposure of workers to high levels of ammonia. In this context, a key issue is the maximum concentration of ammonia allowable in fly ash, below which worker safety would not be a concern. Therefore, an experimental procedure was designed to address this issue. An 11 cm thick layer of ammonia-laden mortar was placed into a 15.2 cm (6 in.) i.d. diameter section of plexiglass pipe that was capped on the bottom. A 213 cm (7 ft) tall section of identical pipe (capped at the top) was then placed over the bottom section and sealed to it using a rubber-lined pipe clamp (Figure 2). The total headspace volume was 41 L above the mortar. Holes were drilled at several locations (10, 40, and 70 in. above the mortar) along the length of the upper pipe section to allow measurement of ammonia concentration inside the pipe (between measurements the holes were plugged). Two of these holes were sometimes used as an inlet and outlet for air ventilation through the pipe in order to test the effects of ventilation rate on the concentration of ammonia in the air. Ammonia concentration of the air within the pipe was measured using Sensidyne and GasTec ammonia detection tubes at specific intervals.

D.3.   Ammonia Loss from Concrete

In order to more realistically study the rate of ammonia loss during mixing, our concrete mixer was modified to closer approximate the dimensions of a commercial concrete truck. Specifically, the end of our mixer was extended approximately 31 cm (12 in) by placing a polyethylene industrial funnel over the mixer opening. The end of the funnel was cut off such that a 15 cm (6 in.) diameter opening remained (Figure 3), and this section of funnel was temporarily sealed to the mixer using duct tape. The procedure commenced with charging the mixer with the ingredients and mixing at 22 RPM for two minutes with the end of the mixer capped to prevent ammonia loss. A sample of concrete (0.5 L) was taken, whereupon the cut-off funnel described above was attached to the mixer, and the mixing speed slowed to 4 RPM which is similar to a Ready Mix concrete truck in-transit to a job site. The concrete was mixed for 40 minutes, with samples taken at 10 minute intervals using a metal scoop. Fly ash "C" was used in all of these tests.

Ammonia was measured in the concrete using an Orion ammonia-sensing gas electrode. The concrete was placed into a 1 L polyethylene bottle, capped, and agitated for 5 minutes. The solid cap was then replaced with a cap in which a 1.9 cm hole had been drilled and fitted with a rubber grommet. The ammonia electrode was inserted into the grommeted hole such that the end of the electrode was above the concrete surface (Figure 4). The ammonia concentration of the water in the concrete was then obtained by comparing the voltage readout with those from standards. The experimental apparatus was checked for accuracy by using cement paste, mortar, and concrete with a known concentration of ammonia. The results of these tests are provided in the Appendix.

After mixing the concrete was placed and compacted into a polyethylene drum that was 40.6 cm (16 in.) in diameter and 15.2 cm (6 in.) high. Concrete was placed into this

section to a thickness of 11cm (4.3 in.), after which section of Sonotube measuring 213 cm (7 ft.) in length was fitted over the base section (containing the concrete) and secured to it using a rubber-lined stainless steel band clamp (Figure 5). Sonotube is a cylindrical cardboard concrete form this is coated internally with wax. In order to inhibit ammonia diffusion out of this tube the interior was coated with additional wax and silicone spray. The Sonotube assembly was designed to represent a cylindrical section of a larger room with a 7.5 ft ceiling height. Ventilation rates were then calculated for the surface area of the concrete slab using ASHRAE recommendations. In this project several ventilation rates were studied. The experimental design also allowed for the measurement of ammonia concentration in the space above the concrete over time, using a similar procedure as was described for mortar (Section D.2 above).

Ammonia that evolved from the concrete was collected in an acetic acid-magnesium acetate aqueous solution and measured using an Orion ammonium ion-selective electrode (Figure 5). This technique is a scaled-up version of the technique used in the mortar experiments. The Sonotube assembly was tested for significant ammonia loss using aqueous solutions of ammonia, and the results of these experiments are provided in the Appendix.

RESULTS AND DISCUSSION
I.   Laboratory Investigations
A.   Unconfined Compressive Strength
Table 7 presents the results of the unconfined compressive strength (UCS) testing for mortar prepared using the different fly ash samples. The data indicate that all of the fly ashes tested pass ASTM C 618 in the context of strength index (minimum 80% of control strength after 7 days). UCS data for concrete cylinders are presented in Table 8, as a function of NH_3 content. It is evident from Tables 7 and 8 that the presence of ammonia has no discernible effect on compressive strength. This result is not unexpected since workers have reported for a number of years that ammonia seems to have no negative impact on concrete strength (e.g. Golden, 2001).

B.   The Rate of Ammonia Loss from Mortar
B.1.   Effect of Mix Proportions
The influence of mix proportioning on ammonia loss rate from mortar was examined using two fly ash samples. In these experiments, the mortar was prepared as described in the Experimental Section. Ammonia was added to the mix water at a concentration of 200 mg NH_3/L solution for both W:CM ratio mortars. This provided the equivalent of 486 mg NH_3 per kg of fly ash for the Low W:CM ratio mortar, and 663 mg ammonia per kg of fly ash for the High W:CM ratio mix. The ammonia concentrations were adjusted in this manner to keep the concentration constant on a solution basis, rather than on an ash basis. Furthermore, all of the ammonia loss data are presented in this report as a fraction of the initial ammonia content because this is the basis that is most useful for estimating the amount of ammonia remaining in mortar and concrete as they cure. Therefore, discussions herein of the rates of ammonia loss from mortar and

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concrete are in reference to the fraction remaining in the material.

The results indicated that the overall ammonia loss rate was slightly greater for the mortar prepared at a higher W:CM ratio. Figure 6 depicts the loss of ammonia as a function of time for mortars prepared using fly ash "R" and "B". Initially, within approximately 24 hrs of the beginning of the experiment, the loss rate was relatively high for both mortars. However, the Low W:CM ratio mortar exhibited a decrease in the loss rate earlier than the higher W:CM ratio material. The result was a greater loss of ammonia in the latter. This was probably caused by a greater quantity of bleed water in the higher W:CM ratio mortar, which would effectively bring ammonia to the surface. In addition, it is well known that an increase in the W:CM ratio, and a decrease in cement content, causes increases in the porosity and coefficient of diffusion of concrete (e.g. Costa et al., 1992; Neville, 1996). Although a well-developed pore system will not have developed within 30 days of curing, the higher water content will have produced a higher "incipient" permeability and porosity. In fact, using a propanol resaturation method described by Day and Marsh (1988), it was determined that the Low W:CM mortar did indeed possess a lower degree of porosity (Table 9).

The mortar experiments also revealed that, unlike aqueous solutions, the rate of ammonia loss occurs in two "stages": a rapid rate followed by a much slower rate that occurred after approximately 24 hours of curing and persisted throughout the remainder of the experiments. Furthermore, at the cessation of the experiment, greater than 80% of the ammonia was calculated to have remained within the mortars. These data indicate that ammonia could continue to evolve from the mortar for a long time after placement, although the rate would be very slow. In fact, at the end of each experiment the mortar cylinders were capped and set aside. After two weeks the ammonia concentration in the 1 L head-space was measured in the "R" mortar samples using detector tubes. The gas concentrations within the cylinders were 60 ppm and 85 ppm for the Low W:CM and High W:CM mortars, respectively, thus confirming that ammonia continued to diffuse out of the mortar.

B.3.   Effect of Fly Ash Source

In this series of experiments six different fly ash samples were used in the preparation of mortar. The rate of ammonia loss from mortars prepared using the six different fly ashes are presented in Figure 7. These data were obtained using the Low W:CM mortar mix and a ventilation rate of 1 L/min. Ammonia was added to the mortars prepared using non-ammoniated fly ash at a concentration of 486 mg NH_3/kg ash. It is evident from the graphs that, in the case of low-calcium Class F fly ash, the source of the ash exerted a negligible influence on the loss rate. However, mortar prepared using the higher-calcium (16% CaO) "R" fly ash evolved ammonia at a slightly slower rate than the Class F ash mortars. This is probably related to the faster rate of strength development (and thus porosity decrease) that occurs when high-calcium fly ash is used in mortar and concrete than when Class F fly ash is used (Thomas et al., 1999). The data also indicate that the origin of the ammonia within mortar exerts a negligible influence on the loss rate. Mortar prepared using non-ammoniated fly ash, with

ammonia added to the water as $(NH_4)_2SO_4$, behaves similarly to mortar prepared using ammoniated fly ash (Figure 7).

B.4. Effect of Ammonia Concentration

The loss of ammonia from mortar as a function of ammonia concentration and at a ventilation rate of 1 L/min is presented in Figure 8. As is expected, the loss rate is greater for mortar containing a higher initial ammonia concentration than for one with less ammonia. However, if the same concentration data are plotted as a fraction of the initial ammonia concentration, it is evident that the rates are similar. This is similar to what is observed in aqueous solutions containing ammonia although, under similar conditions, nearly all ammonia would be lost from water after several days. In contrast, several months would be required to remove even 20% of the ammonia from mortar. A practical application of these data is that, in theory, the quantity of ammonia present in mortar after placement at a specific time can be estimated provided the initial concentration is known. However, as is discussed below, knowledge of the ventilation rate is needed.

B.5. Effect of Ventilation Rate

According to work by Weiler (1979) the rate of ammonia loss from water to the atmosphere is a function of pH, temperature, the area:volume ratio of the water body, and the wind speed passing over the water body. It has been found for seawater that the loss rate to the atmosphere of gases that are reactive in water, such as SO_2 and NH_3, is primarily controlled by resistance in the gas concentration in the air layer immediately overlying the seawater (Hicks and Liss, 1976). Thus, for water with a high pH (i.e. 12), and a constant temperature and area:volume ratio, the ammonia loss rate should be limited by the air ventilation rate over the water. This has practical implications for this project because of the wide range of ventilation conditions that exist during the placement, finishing, and curing of concrete in its wide range of commercial applications.

Figure 9 depicts the effect of ventilation rate on ammonia loss from Low W:CM mortar at 18°C. The data indicate that an increase in ventilation did indeed substantially increase the ammonia loss rate from mortar. Ventilation of the cylinder with 15 L/min of fresh air for four weeks caused a loss of 40% of the ammonia compared with only 15% in the case of the 1L/min ventilation. These data indicate that a well-ventilated space could substantially increase the loss of ammonia from mortar and, by inference, a concrete slab. If a multiple regression is performed on the data, using a 7-parameter exponential decay function (Jandel Sigma Plot), an empirical extrapolation of the ammonia loss after 6 months can be estimated. This is graphically shown in Figure 10, and indicates that, even at the 15 L/min ventilation rate, greater than 50% of the initial ammonia would remain in the 11 cm thick mortar slab after 6 months. This is rather surprising since the 15 L/min rate represents a replacement of air within the cylinder every 4 seconds; for a hypothetical ceiling height of 8 ft. (2.4 m), a fresh air replacement would occur every 3 minutes. The data also suggest that the rate of

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ammonia diffusion from mortar is limited by the gas phase ammonia concentration immediately above the mortar surface and not by diffusion through the mortar.

All of the data and interpretations provided thus far are for 11 cm (4.33 in) thick mortar slabs. It is logical to assume that a thicker slab will retain a greater proportion of ammonia than a thinner slab, due to diffusional limitations through the slab. Therefore, an experiment was conducted to test the effect of mortar thickness on the ammonia loss rate. In this experiment, the loss of ammonia from a 3.5 cm thick mortar slab was compared with that from the "standard" 11 cm thick slab containing the same amount of NH_3 added per kg of fly ash. It was found that, on a fractional basis, the thinner slab lost a significantly higher proportion of ammonia than the thicker (11 cm) mortar slab. However, the total amount of ammonia that diffused from the thicker slab was greater than the thinner slab. This suggests that, although most ammonia is lost from the upper portions of a slab, ammonia from deeper areas also was able to leave the mortar but with greater diffusional limitations. Another interesting aspect of the data is that the ammonia loss from the 3.5 cm mortar slab nearly ceased within 2 months, although there remained greater than 60% of the initial ammonia concentration within the mortar. One explanation for this is that a large quantity of ammonia escaped the mortar during preparation or placement, which is unlikely since the method was tested early in the project (see Appendix). Another is that a large amount of ammonia diffused into the underlying damp sand. Indeed, an ammonia odor was detected in the sand at the cessation of the experiments after the mortar slab was removed from the cylinder. It is more likely that nearly 60% of the initial ammonia remained trapped within the mortar, and would diffuse from the material at a very slow rate over many months.

B.6.   Ammonia Concentration in the Air

When placed in a space with no ventilation, the ammonia concentration was highest near the mortar surface for the first several hours (Table 10). However, after 2 hours the ammonia concentration was homogeneous from top to bottom. This trend was observed for all of the experiments without ventilation, and affirms that the distribution of NH_3 gas in an enclosed space is controlled by diffusion and not gravity i.e. ammonia is lighter than air, but does not accumulate at the highest part of an enclosed space. The data also indicate that the maximum ammonia concentration in the air is, as expected, mainly a function of ammonia concentration in the ash, the proportion of ash in the mix, and the ventilation rate. Figure 11 depicts this relationship for the Low W:CM mortar, prepared using different ammonia concentrations and exposed to various degrees of ventilation. The lines drawn between points for the 0.5, 1.0, and 2.0 L/min ventilation experiments are only illustrative, based on a single data point and an assumed 0 ppm NH_3 in the air for a mortar prepared without any ammonia in the mix. From Figure 11 the maximum permissible ammonia concentration can be estimated for this standard mortar, if the NIOSH TWA limit of 25 ppm is not to be exceeded: in an enclosed space without ventilation, the maximum concentration is 200 mg NH_3/kg ash, whereas for a well-ventilated space (e.g. 2 L/min = fresh air replacement every 21 minutes) the maximum could approach 500-600 mg/kg. As will be shown below, the maximum concentrations for concrete are significantly different.

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The effect of mix proportioning on ammonia-in-air concentration is shown in Table 11. For the first mortar, prepared using fly ash "B" and ammonia added at a concentration of 122 mg/kg ash, the W:CM ratio was increased to 0.66 (the water content was increased as well). In the second test, ammoniated fly ash "Y" (298 mg NH_3/kg) was used in the preparation of the mortars, and one of the mixes contained a mid-range water reducer at a rate of 667 ml per 100 kg of cement + fly ash (10 oz/100 lbs cwt). From the data in Table 11 it is evident that increasing the slump of the mortar mix can increase ammonia evolution from the fresh mortar into the air, even though the High W:CM mortars contained a lower ammonia concentration in the water than the Low W:CM counterparts (from dilution). This effect seemed to be associated with an increase in the quantity of bleed water that occurred at the surface of the mortars, which carried ammonia with it. Furthermore, excessive bleed can introduce channels in the mortar which would provide a conduit for ammonia release. Thus, preparation of a mortar with a high W:CM ratio and water content could actually result in a higher ammonia concentration in the air. This is in contrast to what was found for concrete, which is discussed in the following sections.

C. Ammonia Loss from Concrete
C.1.   Comparison of Concrete and Mortar Data
At the beginning of concrete testing, an experiment was designed with the objective of comparing the rate of ammonia loss from concrete with that from mortar. Because the concrete experiments utilized the Sonotube apparatus, with a 213 cm height (283 L volume) above the concrete, a mortar experiment was conducted using the 40 L (218 cm tall) plexiglass tube assembly that was described in Experimental Section D.2. The concrete and mortar were prepared using the Low W:CM mix proportions, "B" fly ash, and 486 mg NH_3/kg fly ash. The ventilation rates were 8.3 L/min (64 L/min per m^2 of slab area) and 1.1 L/min (60 L/min per m^2 of slab area) for the concrete and mortar, respectively. The results indicated that ammonia diffused from concrete at a faster rate than from mortar over a 1 month period (Figure 12). Although the reason for this is not known, the rate difference is possibly caused by porosity at the cement paste-coarse aggregate interface that is not present in mortar. However, it is also possible that the results from the smaller-scale mortar experiments did not "scale-up" proportionally to the larger-scale concrete experiments which utilized a larger surface area slab, a different mixer, and a higher air ventilation rate.

C.2.   Ammonia Loss During Mixing
The loss of ammonia from concrete during mixing was accomplished as described in the Experimental section. The first set of tests examined the effects of batch size on the ammonia loss rate, based on the hypothesis that a larger batch would contain less free air space above the concrete within the mixer and would thus lose a smaller percentage of the initial ammonia content. Figure 13 presents the results of these tests and shows that batch size did indeed exert a pronounced effect on the ammonia loss rate during mixing. For the 20 L batch, the mixer was approximately ½ full whereas the

40 L batch was near the mixer capacity. As is seen in Figure 13, after 40 minutes of mixing the 20 L batch contained about 65% of the initial NH_3 content, whereas the 40 L batch retained almost 90% of the initial amount. The implication of these data is that a full Ready Mix concrete truck will retain a larger proportion of ammonia than if the truck is not filled to capacity.

Figure 14 presents the results of tests designed to investigate the effects of mix proportioning. For our three concrete mix designs, the Low W:CM concrete lost proportionately less ammonia during mixing than the High W:CM concrete, with the Medium W:CM mix intermediate between the other two. Because the total cementitious content (CF), and thus fly ash content, decreased with an increase in the W:CM ratio, a separate experiment was performed using the Low W:CM mix. For this test a concrete mix was designed with a W:CM = 0.44, but with a lower cementitious content (Table 12) and similar slump. It was found that the lower CF mix lost ammonia at a higher rate during mixing than the higher CF mix, suggesting that the loss rate is dependent on the cementitious content and not only the W:CM ratio (Table 12).

It was observed during the mixing tests that the mixing temperature seemed to have an effect on the results. Specifically, the ammonia loss rate apparently increased with an increase in temperature, particularly after 20-30 minutes mixing. Consequently, data collected at 22°C was compared with those collected at 28°C (Figure 15), which showed that the percentage of ammonia remaining in the concrete at the higher temperature was less than at the lower temperature. However, during the first 20 minutes the data were essentially the same at the two temperatures and did not diverge until the 30 and 40 minute readings. We believe that the observed difference at the two temperatures was largely caused by limitations of the experimental method. Over the course of the experiments it was observed that the data became more inconsistent as the concrete slump decreased, the degree of which is more pronounced at higher temperatures (Klieger, 1958). The stiffer material (i.e. < 3 in. slump) was not as amenable to mixing within the polyethylene bottle and thus we felt that an equilibrium concentration of ammonia in the bottle head space was ever achieved during the analysis. Based on these and other experiments it was concluded that temperature did not exert a significant influence on the rate of ammonia loss from concrete during mixing, but did effect the experimental methodology.

During mixing of concrete that contained ammonia, several interesting observations were made. One unexpected observation was that it was often difficult to smell ammonia coming from the concrete even when standing near the mixer. Typically, one would need to be at the mixer opening in order to detect even a slight ammonia odor. However, the odors inside the drum were often very strong. In two experiments the concentration of ammonia within the mixing drum was measured for concrete containing 50 and 73 mg NH_3 per liter of mix water. In these tests, the ammonia concentration within the drum reached 22 ppm and 35 ppm, respectively for the two mixes, within 5 minutes of the start of mixing. As will be discussed in Section C.5 below, this is substantially less than the concentration measured in the air during and

immediately after placement of the concrete. Similar observations were also recorded during the field tests.

C.3.   Effect of Mix Proportions on the Long-Term Loss Rate

Four separate concrete mixes were prepared to test the effects of mix proportioning on the rate of ammonia loss during 1 month curing. In addition to the three mixes listed in Table 6, an additional mix was prepared. It is common for water to be added to Ready Mix concrete when it arrives on a job site, in order to increase the slump and make the concrete easier to work, although the strength and durability are lowered. Therefore, the additional mix was prepared by adding AEA, no mid-range water reducer, and enough water to the Low W:CM mix to achieve a W:CM = 0.50. The slump of this mix was approximately 203 mm (8 in). Figure 16 shows the ammonia loss rate from the four different concrete mixes, expressed as a fraction of the initial NH_3 concentration in the concrete. The data indicate that the different mix proportions had no significant effect on the fraction of NH_3 remaining in the concrete after 1 month, which was approximately 65-70% of the initial amount. These data are inconsistent with the mortar data which indicated that the High W:CM ratio mortar lost ammonia at a greater rate than the Low W:CM mortar. However, as was discussed above the difference was probably related to the greater quantity of bleed water that was observed for the High W:CM mortar. In comparison, even the High W:CM (0.68) concrete mix did not exhibit nearly the degree of bleed observed for the High W:CM mortar.

The data presented in Figure 16 were calculated based on the initial ammonia present in the concrete at the onset of mixing. It was shown in Section C.2 that the loss of ammonia during mixing depends on the mix proportions, with the High W:CM mix losing a greater fraction of ammonia than the Low W:CM mix. The data in Figure 16 do not account for the difference in ammonia concentration in the concrete, after mixing for 2 minutes, at the start of the month-long experiments. Therefore, the data were "corrected" to account for the mixing losses, and the new ammonia loss curves presented in Figure 17. It is evident that, although the 0.68 and 0.55 W:CM concrete lost ammonia at a higher rate than the 0.50 and 0.44 W:CM mixes, the differences are slight.

Using a technique similar to the mortar data, the ammonia loss rate data for concrete was extrapolated to four months time (Figure 18). These calculated data suggest that after approximately 2 months the loss rate had slowed dramatically, whereupon greater than 60% of the initial ammonia remained in the concrete. Accounting for losses during mixing and some escaped ammonia from the apparatus, as a general rule, greater than 50% of the initial ammonia is expected to remain in a 4 - 5 inch thick indoor concrete slab after several months of curing. After that, the remaining ammonia will probably take many months to diffuse from the concrete slab. For thicker slabs, a higher percentage of the ammonia will likely remain.

C.4.   Effect of Ventilation Rate on the Long-Term Loss Rate

In a separate set of experiments, another departure from the mortar data was

observed: ventilation rate apparently exerts a negligible influence on long-term ammonia loss rate from concrete. Two experiments were conducted using the Medium W:CM mix prepared using fly ash "C", with ventilation rates of 8.3 L/min and 15.2 L/min through the Sonotube apparatus. As can be seen in Figure 19 these ventilation rates produced similar ammonia loss rates over the course of 1 month. It should be noted that ventilation rates of 8.3 and 15.2 L/min represent an exchange of the air within the Sonotube every 33 and 19 minutes, respectively. It appears that, under these ventilation conditions, the diffusion of ammonia from concrete is limited by the rate of mass transfer through the concrete and not by dissipation of the gas phase ammonia above the concrete, as is the case for water. Therefore, according to our data the placement of concrete outdoors, with a high degree of ventilation, prior to enclosure within a structure would not necessarily result in an increased loss of the ammonia within the concrete compared with a slab placed indoors with a lower degree of ventilation.

C.5.   Ammonia Concentration in the Air

The concentration of ammonia in the air above fresh concrete was first measured for the conservative case of no ventilation through the Sonotube apparatus. It was observed in each of these experiments that after placing the concrete, the ammonia in the air increased steadily to a maximum concentration within 2-3 hours, followed by a gradual decrease (Figure 20). Although there was no ventilation within the Sonotube, and thus the ammonia should not have decreased, it was not completely air-tight. Thus, some ammonia was able to slowly escape during the experiment (this was not deemed to be a problem for the long-term experiments because air was being *pulled through* the Sonotube and therefore should keep any significant amount of ammonia from leaking out of the apparatus). In the experiments where Sonotubes were vented with 8.3 and 15.2 L/min fresh air, a significantly different profile was observed for ammonia buildup in the air. In these cases, the ammonia concentration in the air increased rapidly to its maximum within approximately 0.5 hrs, whereupon it decreased rapidly (Figure 21). The increased fresh air ventilation not only lowered the ammonia concentration in the air (described below) but also shortened the time required for the ammonia to be evenly distributed in the headspace.

The experiments described above were conducted using the three different W:CM ratio concrete mixes, using both ammoniated and non-ammoniated fly ash, and with different ammonia concentrations. In addition, several experiments were conducted using ammoniated fly ash at a cement replacement of 30% instead of 20%. This had the effect of increasing the NH_3 concentration in a different manner than adding more ammonia to the water or decreasing the W:CM ratio. The maximum ammonia concentration in the air was then recorded for each experiment (generally after 3 hrs for the non-ventilated experiments, and 0.5 hours for the ventilated ones) and compared with the ammonia concentration of the fly ash (Figure 22) (for non-ammoniated fly ashes, where ammonia was added to the water, the concentration is also expressed on an ash basis). The graph in Figure 22 reveals an obvious relationship between the

ammonia concentration in the fly ash and the maximum concentration of ammonia in the air. There is, however, a significant degree of scatter in the data, particularly at high ammonia concentrations. Furthermore, there is very little difference between the ventilated and non-ventilated experiments. Although a part of the scatter can be attributed to experimental error, some of it is caused by reporting the ammonia concentrations on an ash basis. This occurs because expressing the ammonia concentrations in this way does not account for the different water contents, W:CM ratio, and fly ash replacement rates that will change the quantity and concentration of ammonia in a concrete mix.

It is more relevant to express the ammonia concentration on a water basis, that is, in mg NH_3/L mix water because it is the ammonia concentration in the water that controls the equilibrium concentration in the air. Plotting the data in this manner (Figure 23) provides a clearer relationship between the variables. Also, the ventilated conditions produce a clearer lower maximum ammonia concentration in the air than the non-ventilated conditions. Interestingly, increasing the ventilation rate to 15.2 L/min (equivalent to a fresh air replacement every 19 minutes) had only a small effect on the maximum ammonia concentration in the air (Figure 23).

An important aspect of the data in Figure 23 is that they provide the information needed to estimate the concentration of ammonia in fly ash that should not be exceeded in order to minimize worker complaints when placing and finishing concrete. The data indicate that for concrete placed in areas with negligible air ventilation the ammonia concentration in the concrete should not exceed 110 mg/L if the recommended exposure limit TWA of 25 ppm is not to be exceeded. However, in the majority of applications there will be some ventilation present. In these cases, the level of ammonia in the concrete should be less than about 170 mg NH_3/L. The maximum permissible concentration of ammonia in the fly ash will therefore depend on the concrete mix proportions. The pertinent equation is then:

$$NH_{3water} = \frac{(NH_{3ash} \times FA)}{WF}$$

Where NH_{3water} is in mg/L, NH_{3ash} is in mg/kg, FA = unit fly ash content, and WF = unit water content.

As an example of the use of this equation, the maximum concentration of ammonia in fly ash is calculated here for a "typical" concrete with 326 kg/m^3 (550 lb/yd^3) of cementitious material, a water:cementitious (W:CM) ratio of 0.50, and a 20% fly ash replacement rate. It follows that for this mix, the ammonia concentration in the ash should not exceed 275 mg NH_3/kg for the relatively rare applications where concrete is placed in a space with negligible ventilation, and 425 mg/kg for the more common case with some degree of ventilation. Obviously, the recommended maximum ammonia in the fly ash would decrease if a greater proportion of fly ash and/or a lower W:CM ratio is used.

Although a TWA of 25 ppm NH_3 in the air is considered safe, it would nonetheless produce a very strong, objectionable odor. Thus, in practice, a lower ammonia-in-air concentration is likely to be followed in order to minimize worker complaints. Assuming a more comfortable threshold of 10 ppm ammonia in the air, the maximum concentration in the concrete water would be approximately 50 and 75 mg NH_3/L for non-ventilated and ventilated conditions, respectively. Using the example and equation above, the maximum ammonia concentration in the fly ash would then need to be 125 and 188 mg NH_3/kg ash for the two ventilation conditions. Results of sample calculations for our Low and High W:CM concrete mixes, with a 20% replacement of fly ash for cement, are presented in Table 13.

C.6.   Comparison with Previous Data

Until this project, probably the most thorough studies had been completed in Europe by Koch and Prenzel (1989) and van der Brugghen et al. (1995). The focus of both of these studies was on the concentration of ammonia in the air during and soon after the placement and finishing of concrete screed and mortar. Comparison of the data from these studies is somewhat problematic for several reasons. The authors studied materials prepared without coarse aggregates (or at least with smaller top size than in our study), although neither study provides information on the aggregate properties. In our study, differences were observed in the ammonia release characteristics from concrete versus mortar. In addition, no information was provided in the European studies on ventilation conditions or the dimensions of the rooms in which the screeds and mortars were placed.

Koch and Prenzel studied concrete screed prepared using both non-ammoniated and ammoniated fly ash. When using ammoniated fly ash and ash that was "spiked" with ammonium bisulfate, the concentration of ammonia in the rooms remained below 7 mg/m^3 and odors were barely noticeable, even when the ammonia concentration was 314 mg/kg of fly ash. Furthermore, there was no clear relationship between ammonia concentration in the concrete screed and that in the air. However, when ammonium chloride was added to the mix water, the ammonia concentration in the air exceeded 95 mg/m^3 in the case where the ammonia concentration in the screed was the equivalent of 300 mg NH_3/kg of fly ash. The reason for this discrepancy is not known. These data are in contrast to our results (Figure 24) where there was a consistent positive relationship between ammonia concentration in the concrete and that in the air.

The van der Brugghen et al. (vdB) study examined ammonia in the air during mixing and placement of concrete mortar as well as the emission of ammonia during the manufacture of synthetic aggregate. In the case of concrete mortars, vdB studied ammonia accumulation in a room open to natural ventilation and two rooms that were closed. When placing concrete mortar (with an ammonia content in the ash of 300 mg/kg) in the open room, the odor of ammonia was only noticed near the floor and was generally between 5 to 10 mg/m^3. When placing the concrete mortar in the closed rooms there was a positive relationship between ammonia concentration in the concrete and that in the air, similar to our results (Figure 24). However, when compared directly,

our results indicated a lower maximum concentration of ammonia in the air for an equivalent concentration of ammonia in the concrete. The differences could be caused by differences in the composition of the concretes (i.e. top size of the aggregates, aggregate proportions) and/or by the ammonia measurement techniques. The vdB study used a spectrometer to measure ammonia in the air, whereas we used an electrochemical ammonia monitor (that gave erroneously high results) and GasTec ammonia sensing tubes, which were more accurate. Furthermore, van der Brugghen et al. reported concentrations at times as mg/m^3 and other times as ppm; these are not equivalent units. Despite some of the differences, a key similarity between the vdB study and our study is that the ammonia concentration in the air decreased to below olfactory detection within 1-2 days, making the potential for long term odors unlikely. In addition, both studies observed that the highest ammonia-in-air concentrations occurred within the concrete and mortar mixers.

C.7   Controlled Low-Strength Material (CLSM)

CLSM is a self-compacting cementitious material used primarily as a backfill, which typically has a compressive strength of less than 300 PSI (ACI, 2000). A key component of CLSM is fly ash, which is often utilized in proportions exceeding 178 kg/m^3 (300 lb/yd^3). In fact, some CLSM proportioning specifies only fly ash and water. It is the high proportion of fly ash in this material that causes concern regarding the utilization of ammoniated fly ash. Although the vast majority of CLSM applications are outdoors, there are instances where the material could be used in a more enclosed space. Furthermore, during the operation of backfilling a trench there might be occasions where workers need to be in the trench for a brief time, for example if a problem occurs during the backfilling. For this reason several experiments were conducted using CLSM, wherein the concentration of ammonia in the air above the material was monitored immediately after placement. The mix proportions were taken from Mix 8 in Crouch et al. (2001), and comprised 36 kg/m^3 cement, 220 kg/m^3 fly ash, 1506 kg/m^3 sand, and 297 kg/m^3 water.

As a "worst case scenario", one experiment was conducted within the Sonotube without any ventilation, using fly ash "B" and an equivalent of 122 mg NH_3 per kg of fly ash added as ammonium sulfate. This produced a concentration in the mix water of 90 mg NH_3/L. Within several hours of the beginning of the test, the ammonia concentration within the Sonotube reached 35 ppm. Compared with the results using concrete (Figure 23), the ammonia concentration in the air above the CLSM was considerably higher at an equivalent ammonia concentration in the mix water. This is similar to what was observed with mortar, and is probably caused by the large quantity of water that bled to the surface of the CLSM. The bleed water effectively transferred a large quantity of ammonia to the surface, which resulted in less diffusional resistance than occurred within concrete. Thus, the combination of a large proportion of fly ash in the mix and a large quantity of bleed water indicated that, in an enclosed space, it is desirable to have less ammonia in the fly ash for CLSM than would be acceptable when the fly ash is used in concrete. However, in several experiments where the top of the Sonotube was removed, in order to simulate an open trench backfill, the ammonia

concentration in the air never exceeded 5 ppm within the Sonotube even when fly ash "C" (280 mg/kg) was used. Therefore it was concluded that for the majority of CLSM applications the presence of reasonable concentrations of ammonia in the fly ash (such as were recommended for concrete) should not present undue safety concerns, although there likely will be noticeable ammonia odors at the job site.

II.   Large-Scale (Field) Investigations
A.   Equipment and Materials

The concrete used in the field testing was purchased from a local Ready Mix concrete plant. Four batches of concrete were obtained and their proportions are provided in Table 14. An AEA and mid-range water reducing admixture were used. In addition, a set retarder was added because of the high ambient temperatures experienced during concrete placement. Concrete for Pours #1 and #2 contained fly ash supplied by the Ready Mix plant, and ammonia was added as ammonium sulfate to the mix water. Concrete used in Pours #3 and #4 contained "C" and "BC" fly ash, respectively, both of which were added to the truck mixing drum prior to charging the other materials.

The concrete truck used was purchased by the CAER and had an 6.5 m^3 (8.5 yd^3) capacity (Figure 25). The first batch of concrete (Pour #1) was obtained with the purpose of "conditioning" the mixing drum (after years of being unused) and practicing our ammonia measurement techniques with large quantities of concrete. This batch was placed as a 10 cm (4 in) thick slab on CAER property (Figure 26). The remaining three batches were placed as slabs inside of vinyl storage buildings, that were 3 m X 4.6 m (10 ft. X 15 ft.) in floor area (Figure 27). Each building was constructed upon 10 cm (4 in.) blocks in order to elevate the base off the ground, and was built inside a 10 cm high steel concrete form perimeter (Figure 28). This allowed for the concrete building slab to be poured in an enclosed environment for ammonia monitoring.

Ammonia loss during mixing was monitored using the same techniques as that used for the laboratory experiments. After the ingredients were charged into the truck mixing drum, the concrete was mixed at high speed for 3 minutes. At this point a sample of the concrete was taken and placed into a 4 L polyethylene bottle for measurement of ammonia concentration. After this initial sample, the concrete batch was mixed at low speed and transported to the CAER site, and additional samples were taken at approximately 10-15 minute intervals both before and during discharge.

The concrete was placed and finished inside the buildings using standard techniques. During this part of the operation, plastic curtains were attached over the door opening to restrict air circulation (Figure 29).

During and after placement and finishing of the concrete, the ammonia concentration within the buildings was monitored using several techniques. GasTec tubes (described above) were used for "spot checks" of the ammonia levels in the air, whilst an ammonia detector/datalogger was used to continuously monitor the concentration over time. The monitor selected was a Draeger Pac III monitor with an ammonia detector module,

combined with a small external battery-powered pump (MiDan Corp.) to pull air across the monitor (Figure 30). Although the monitor specifications do not indicate it, the monitor was very sensitive to humidity and temperature changes and was thus difficult to calibrate for the conditions encountered during actual use. Therefore, the Draeger monitor data presented herein are useful only to show the trend of ammonia concentration in the air with time; absolute concentrations had to be corrected based on the GasTec tube data.

Specific information on each of the field experiments are presented below.

B.   Concrete Pours
Pour #2 (Storage Building #1; 26June02)
The concrete for this test was prepared using non-ammoniated fly ash, with ammonium sulfate added to the mix water to achieve a concentration of 83 mg NH_3/L water. The loss of ammonia from the Ready Mix truck was not monitored for this pour because of problems that occurred during mixing. During placement of the concrete, the maximum concentration of ammonia in the storage building reached 13 ppm; this maximum concentration was achieved within ½ to 1 hour. Within 24 hours, the concentration in the air was below 1 ppm. During this experiment, there were no safety concerns encountered regarding exposure to ammonia. The only location where high levels of ammonia were encountered were at the discharge point of the concrete mixing drum. During mixing, the ammonia concentration in the air at the discharge opening was checked using the GasTec tubes, and exceeded 30 ppm in one measurement. It can be inferred from these data that the ammonia in the concrete mix could reach equilibrium with that in the air within the drum, which in this case would approach 80 ppm. However, this should not cause undue concern since it is unlikely that anyone could (or would want to) get inside the drum when it contains concrete.

Pour #3 (Storage Building #2; 16July02)
In this test, fly ash "C" (280 mg NH_3/kg ash) was used in the concrete. The loss of ammonia during mixing is shown in Figure 31, and was consistent with laboratory data. The ammonia concentration within the storage building increased to a maximum of approximately 20 ppm within an hour after beginning the placement of the concrete slab. Thereafter, the ammonia level decreased steadily to less than 5 ppm after 1 day, was less than 1 ppm after 3 days, and less than ½ ppm after 7 days (Figure 32). The high concentration of ammonia in this ash undoubtedly caused the prolonged higher concentrations in the air compared with Building #1. Similar to Pour #2, the concentration of ammonia at the discharge end of the mixing drum exceeded 30 ppm in one measurement and was the only location where high ammonia levels were encountered in the air.

Pour #4 (Storage Building #3; 24July02)
In this experiment, fly ash "BC" (90 mg NH_3/kg ash) was used in the concrete. The ammonia loss during mixing is shown in Figure 31 along with data from Building #2.

These data suggest that the mixing losses were similar for Pour #3 & #4, and were in agreement with laboratory data (Figure 33). The ammonia concentration within Building #3 reached a maximum of 6 ppm within the first ½ hour of placement and finishing (Figure 34). The following morning the ammonia level was 2-3 ppm in the building, and decreased to less than 1 ppm by the next day (Figure 34). The highest concentration of ammonia in the air was again measured at the discharge opening of the mixing drum, and was as high as 17 ppm in one instance.

In general, the maximum ammonia levels recorded in each of the buildings typically occurred within ½ to 1 hour after the start of the test and were in good agreement with the laboratory data discussed above. Comparison of the two sets of data is provided in Figure 35. The degree of ventilation in each building varied during placement due to occasional wind gusts, but was generally low because of the plastic curtains covering most of the door opening. However, the ventilation was certainly greater than the laboratory experiments conducted wherein the Sonotube apparatus was completely sealed. Thus it was expected that the field test data would plot close to the laboratory data obtained with 8.3 L/min or 15 L/min ventilation through the Sonotube. From Figure 35 it is evident that the prediction was fairly accurate. More importantly, the large-scale testing data support the interpretations based on the laboratory data; specifically, that for most applications the estimated maximum concentration of ammonia in the concrete is 170 mg/L, if an ammonia concentration of 25 ppm is not to be exceeded in an enclosed workspace. For those areas with negligible ventilation, 110 mg/L should probably not be exceeded in the concrete. From this and the knowledge of the concrete mix proportions, the maximum permissible ammonia in fly ash can be calculated.

CONCLUSIONS
The objective of this study was to develop rule of thumb guidelines for the utilization of ammoniated fly ash in mortar and concrete, by gaining a more thorough understanding of the behavior of ammoniated ash in these materials. Foremost amongst the concerns with using ammoniated fly ash is the maximum amount of ammonia in fly ash, below which worker safety would not be compromised. NIOSH recommends a TWA concentration in the workplace of 25 ppm in the air, and a STEL of 35 ppm.

Results of this study indicate that the maximum concentration of ammonia in fly ash primarily will depend on concrete mix proportions and the degree of ventilation present where the concrete is being placed. For the concrete prepared in this study, with a W:CM range of 0.44 to 0.68, the maximum "acceptable" ammonia concentration in the fly ash was surprisingly high, even when there was essentially no ventilation. Under these conditions, and with a 20 % replacement of fly ash for cement, it is estimated that the ammonia in ash could be as high as about 240 to 375 mg NH_3/kg of ash for the Low and High W:CM mixes, respectively. In commercial applications, placing concrete in an enclosed space with no ventilation is probably a relatively uncommon occurrence compared with applications where there is some ventilation present. For these more common concrete uses, the maximum acceptable ammonia concentration would be

between 375 and 575 mg NH_3/kg of ash, for our Low and High W:CM concrete mixes. When using a greater percentage of fly ash in the mix, the acceptable concentration will decrease. In actual practice, however, an ammonia concentration in the air below the NIOSH TWA is likely to be targeted because 25 ppm ammonia does produce a very noticeable odor. From experience gained in this study, a concentration of 10 ppm in the air is more comfortable to work with. If 10 ppm is used as a "marketable exposure limit", then the permissible ammonia concentration in the fly ash will be less than if the NIOSH air limits are followed. The ammonia concentration in fly ash that will result in 10 ppm or less ammonia in the air can then be calculated from the equation provided in this report if the concrete mix proportions are known.

As a general rule, it was determined that about 15% of the initial ammonia content in concrete was lost after 40 minutes of mixing, although the percentage lost depended on the mix proportions and the batch volume i.e. a full mixer lost less than a partially full mixer. When placing the concrete in an enclosed space it was found that the ammonia loss rate from the concrete decreased substantially after 1 month, although greater than 50% of the initial ammonia was calculated to have remained in the 11 cm thick concrete (a greater percentage would remain in a thicker slab). The remaining ammonia would diffuse from the concrete at a very slow rate over the course of many months. However, this is not likely to result in any long-term ammonia odors in enclosed spaces (e.g. residential basements) because our data showed that the ammonia concentration in the air was below 1-2 ppm after several days curing, even when the fly ash contained high levels of ammonia. Thus it is likely that the major concern with using ammoniated fly ash in mortar and concrete will be odors present during placement and finishing, that is, within the first three to four hours.

The long term loss rate of ammonia from concrete was not affected by mix proportions or ventilation rate, which suggests that the ammonia diffusion rate was limited by mass transfer through the concrete and not by dissipation of the gas phase above the concrete. This was not the case for mortar, where a higher W:CM ratio, water content, and ventilation rate caused an increase in the ammonia loss rate. Interestingly, after 1 month curing a substantially greater percentage of ammonia remained in the mortar compared with concrete when equivalent ventilation rates were used.

The final phase of the project involved commercial scale utilization of ammoniated fly ash in concrete. The maximum concentration of ammonia in the air within the buildings during placement and finishing agreed well with laboratory data, as did the quantity of ammonia lost during mixing. In general, during the mixing and placement of ammonia-laden concrete, no safety concerns were encountered even when a fly ash containing 280 mg NH_3 per kg of fly ash was used. The only location where the ammonia concentration attained high levels (i.e. > 25 ppm in the air) was within the concrete mixing drum.

RECOMMENDATIONS FOR FUTURE RESEARCH
Overall, this project succeeded in providing a better understanding of the behavior of

ammoniated fly ash in mortar and concrete, and in developing some guidelines for use. However like many research projects, many questions remain unanswered, and the experimental results produced new questions. One fundamental question that remains involves the effect of temperature on the loss rate of ammonia from mortar and, in particular, concrete during mixing and curing. One of the problems encountered with the temperature control of concrete involved the scale of the work. In order to precisely control the temperature during these experiments the apparatus devised must be large enough to encompass a concrete mixer, several fairly large (e.g. 16 in diameter) concrete slabs, and the 7-8 ft head-space above the slabs. However, experiments of this nature would be important to understanding the diffusion behavior of ammonia through concrete and mortar.

Another practical problem is the effect of humidity on the ammonia loss rate. Studies of oxygen and carbon dioxide diffusion through concrete and mortar indicate that humidity can lower the diffusivity rate because water in the pores inhibits transfer of the insoluble gases through the material (e.g. Houst and Whitman, 1994). However, the high solubility of ammonia gas may result in humidity having less of an influence. A potential effect would be a case where the humidity is low in a residential space whilst the concrete is in contact with moist soil or aggregate. In this situation it is possible for a "wicking effect" to occur, which would bring ammonia through the concrete. Although a fundamental examination of ammonia diffusion, at first glance, would not appear to provide practical information regarding the release of ammonia from mortar and concrete, such a study would provide valuable information on the environmental variables that affect the ammonia diffusion rate through the materials. If a study of diffusion did establish that humidity and temperature affect the diffusivity rate, it would still need to be ascertained if the effects are significant and thus observable in practice.

Another useful study would involve testing the conclusions and recommendations offered herein by conducting additional large-scale experiments such as were conducted at the end of this project. To accomplish this it would be necessary to team with a Ready Mix plant and contractors that are willing to work with ammoniated ash. The ammonia concentration in the workplace during concrete placement and finishing could be monitored and the data compared with the results of this study. This work would need to be completed in the near future in advance of the installation of many more SCR and SNCR systems.

Finally, it would be of use to the ash marketing industry for a technical and economic assessment to be made of the various existing ammonia removal (from fly ash) processes. Similarly, a high priority should be given to the development of inexpensive ammonia removal or "passivation" processes that are compatible with current ash handling systems and processes, either at the power plant or the Ready Mix operation.

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Table 1. Source and General Information for Fly Ash Samples

Sample	Location	Ammonia Injection	Coal Type
B	Georgia	None	Central App. Bit.
MC	Kentucky	None	Northern App. Bit.
R	Indiana	None	App. Bit./Subbit. blend
C	Ohio	ESP Conditioning	Northern App. Bit.
BC	North Carolina	ESP Conditioning	Central App. Bit.
Y	Georgia	ESP Conditioning	Central App. Bit.

* App. Bit. = Appalachian, Bituminous rank, Subbit. = Subbituminous rank

Table 2. ASTM C 618 Data for Fly Ash Samples

Sample	Moisture (%)	LOI (%, dry)	SO3 (%, dry)	Si+Al+Fe (%, oxides)	+325 Mesh (%, dry)
B	0.1	2.1	0.3	89.4	19.9
MC	0.1	1.7	0.8	88.1	21.4
R	0.1	0.9	0.7	70.3	20.4
C	0.1	1.2	0.4	89.3	19.5
BC	0.1	4.3	<0.1	92.9	33.9
Y	0.1	8.1	0.1	92.0	29.0

Table 3. Chemical Composition of Fly Ash Samples

Sample	C (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	NH_3 (mg/kg ash)
B	1.5	54.5	28.3	6.6	2.4	1.2	0.4	2.5	1.1	0
MC	1.5	49.5	20.7	17.8	4.3	1.0	0.5	2.8	1.1	0
R	0.7	42.3	22.7	5.3	16.0	4.0	1.4	1.2	1.4	0
C	0.7	45.8	24.3	19.2	2.4	0.8	0.4	1.9	1.3	280
BC	4.0	55.2	31.9	5.8	0.8	0.8	0.4	2.1	1.9	90
Y	6.8	53.7	27.0	11.3	1.9	1.3	0.5	3.1	1.4	298

Table 4. Aggregate Testing Data

Aggregate Type	Moisture (%)	Sp.Grav. (SSD)[1]	Absorption (%)	Unit Wt. (kg/m^3)	Top Size (mm)	Fineness Modulus
Fine	4.4	2.63	1.54	na	4.75	2.77
Coarse	0.1	2.71	0.43	1561	25	na

[1]SSD = saturated, surface dry condition

Table 5. Mortar Mix Proportions

Property/Component	UCS Mix	Low W:CM Mix	High W:CM Mix
Cement (g/L)	543	429	392
Fly Ash (g/L)	124	107	98
Sand (g/L)	1,226	1,475	1,349
Water (g/L)	314	260	324
W:CM	0.471	0.485	0.661
Yield (L)[1]	1.002	1.000	1.000

[1]Assumes component specific gravities: cement = 3.15, fly ash = 2.40, sand = 2.64, water = 1.00

Table 6. Proportions of Concrete Mixes Used in this Study

Property/Component	Low W:CM Mix	Med W:CM Mix	High W:CM Mix
Cement (kg/m^3)	354	245	203
Fly Ash (kg/m^3)	88	61	51
Fine Aggregate (kg/m^3)	792	862	873
Coarse Aggregate (kg/m^3)	1000	1070	1090
Water (kg/m^3)	195	168	173
Water:Cement + Fly Ash	0.44	0.55	0.68

Slump (mm, in.)
    no admixtures
    with admixtures[1]
	76, 3
	127, 5
		no data
		178, 7
			76, 3
			178, 7

Air Content (%, volume)[2]	5.5	6	6

[1] Low W:CM mix = 3.25 ml X20/kg cement + fly ash, 3.25 ml Air 40/kg cement + fly ash
High W:CM mix = 0.65 ml Air 40/kg cement + fly ash
[2] Air content determined only for concrete mix containing the admixtures

Table 7. Unconfined Compressive Strength (UCS) of Mortar

Fly Ash Used in Mortar	7-Day UCS (PSI)	7-Day % of Control	28-Day UCS (PSI)	28-Day % of Control
OPC Only	4330	100	5700	100
B	4140	96	5560	98
MC	4400	102	6040	106
R	4670	108	5810	102
C	4070	94	5630	99
BC	4270	99	6120	107
Y	3900	90	5450	96

Table 8. UCS of Mortar with Added Ammonia

Fly Ash Used In Mortar	Ammonia Concentration (fly ash basis)					
	0 mg/kg Ammonia		100 mg/kg Ammonia		200 mg/kg Ammonia	
	7-Day	28-Day	7-Day	28-Day	7-Day	28-Day
B	4140	5560	4580	5550	4230	5610
MC	4400	6040	4370	5700	4760	5300
R	4670	5810	4630	5820	4720	5730

Table 9. Porosity of Low and High W:CM Mortars

Fly Ash Used	Low W:CM Mix	High W:CM Mix
R	13.0 %	17.1 %
B	13.4 %	18.8 %
MC	14.1 %	18.2 %

Table 10. Ammonia in Air Above Fresh Mortar:
122 mg NH$_3$/kg ash, no ventilation

Time (hrs)	Ammonia Concentration in the Air (ppm)		
	Bottom	**Middle**	**Top**
0	0	0	0
0.5	11	10	7
1	16	14	12
2	16	16	16
6	17	17	17
22	12	12	13
52	9	9	9

Table 11. Maximum Ammonia Level in Air Above Fresh Mortar

Ammonia Concentration	Low W:CM Mix	High W:CM Mix	Low W:CM Mix w/ Mid-Range
122 mg NH$_3$/kg ash	16 ppm	20 ppm	--
298 mg NH$_3$/kg ash	38 ppm	54 ppm	55 ppm

Table 12. Ammonia Loss During Concrete Mixing: Effect of Cement Content

Concrete Mix	Percentage of Initial NH$_3$ in Concrete				
	Initial	**2 min.**	**10 min.**	**20 min.**	**30 min.**
Low CF	100	100	92	83	73
High CF	100	98	98	91	88

Table 13. Estimated Maximum Quantities of NH$_3$ in Fly Ash for Two Concrete Mixes Used in This Study, Based on an NH$_3$ in Air Concentration of <25 ppm[1]

W:CM Ratio of Concrete	Maximum NH$_3$ in Fly Ash (mg/kg)	
	No Ventilation	Ventilation Present
0.44	244	377
0.68	373	577

[1] For concrete to be placed in an enclosed space

Table 14. Proportions of Concrete Used for Large-Scale Experiments

Property/Component	Pour #1	Pour #2	Pour #3	Pour #4
Cement (kg/m^3)	218	217	231	224
Fly Ash (kg/m^3)	62	66	72	68
Fly Ash Replacement (%)	22	23	24	23
Fly Ash Source	Plant[1]	Plant[1]	"C"	"BC"
Fine Aggregate (kg/m^3)	806	817	842	840
Coarse Aggregate (kg/m^3)	1100	1101	1095	1106
Water (kg/m^3)	141	137	151	151
Batch Size (m^3)	1.14	3.06	3.34	3.36
Water:Cementitious	0.50	0.49	0.50	0.51
Slump (cm)	15	7.5	15	10

[1] Ready Mix plant supplied Class F fly ash
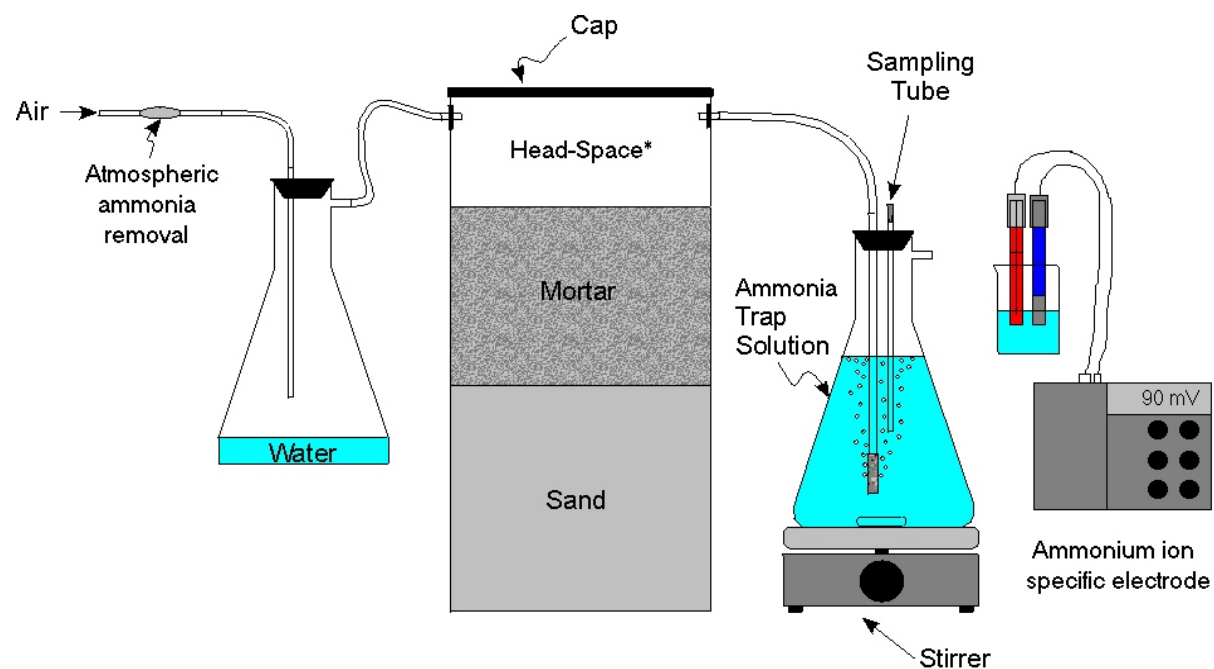
*For some experiments the space above the mortar layer was increased from 5.5 cm to 225 cm high to represent a column of air in a residential basement

Figure 1.   Experimental apparatus used to measure the rate of ammonia loss from mortar.
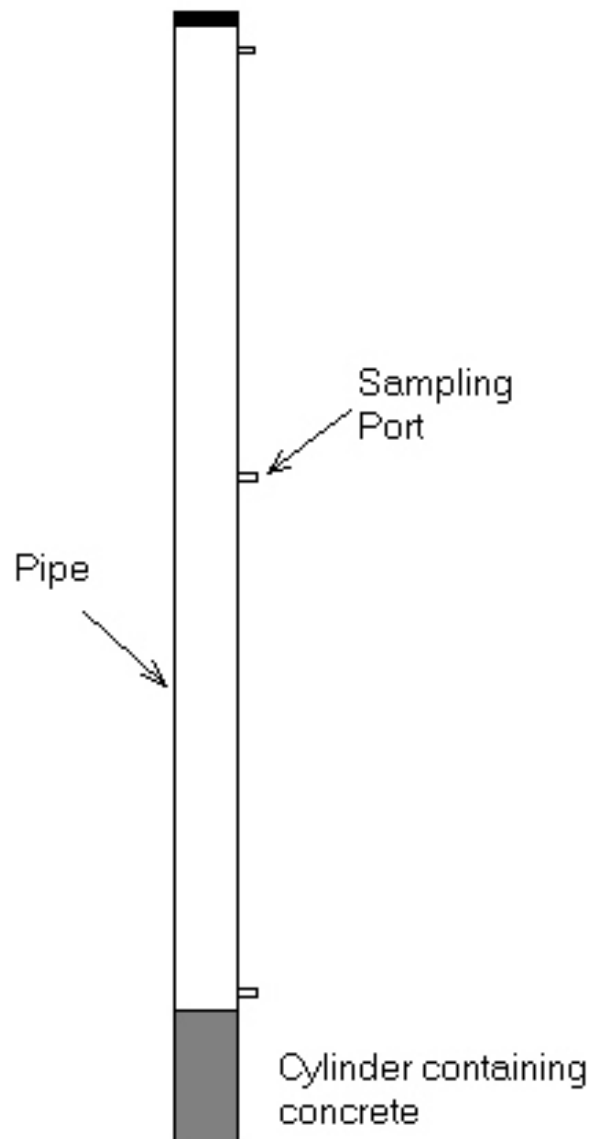
Figure 2.   Apparatus designed to measure the concentration of ammonia in the air above mortar.

Figure 3.   Concrete mixer modified to approximate the dimensions of a Ready Mix truck mixing drum.
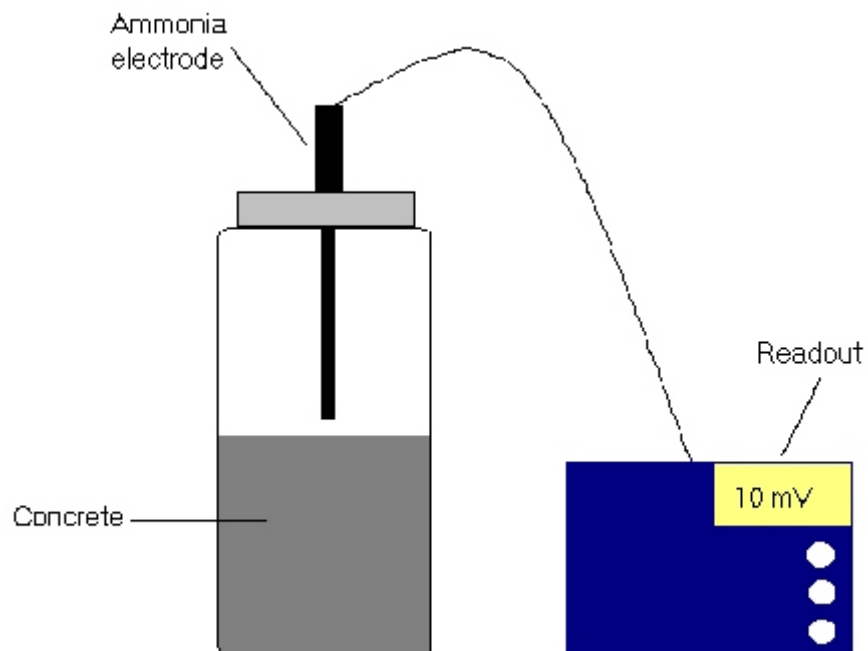
Figure 4.   Apparatus used to measure the ammonia concentration in fresh concrete.
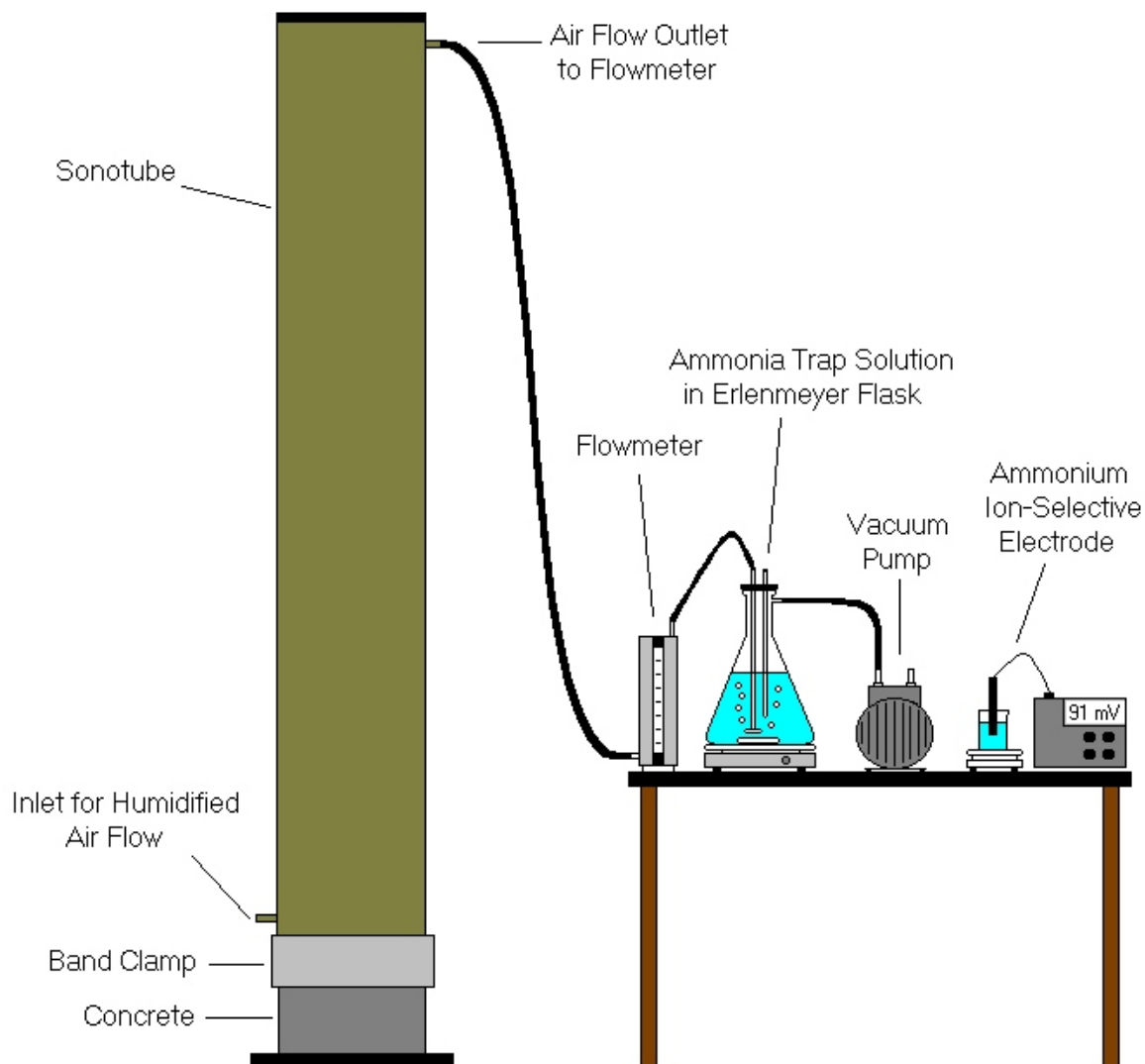
Figure 5.   Apparatus used to measure the ammonia loss rate from concrete, and the concentration of ammonia in the air above a concrete slab.
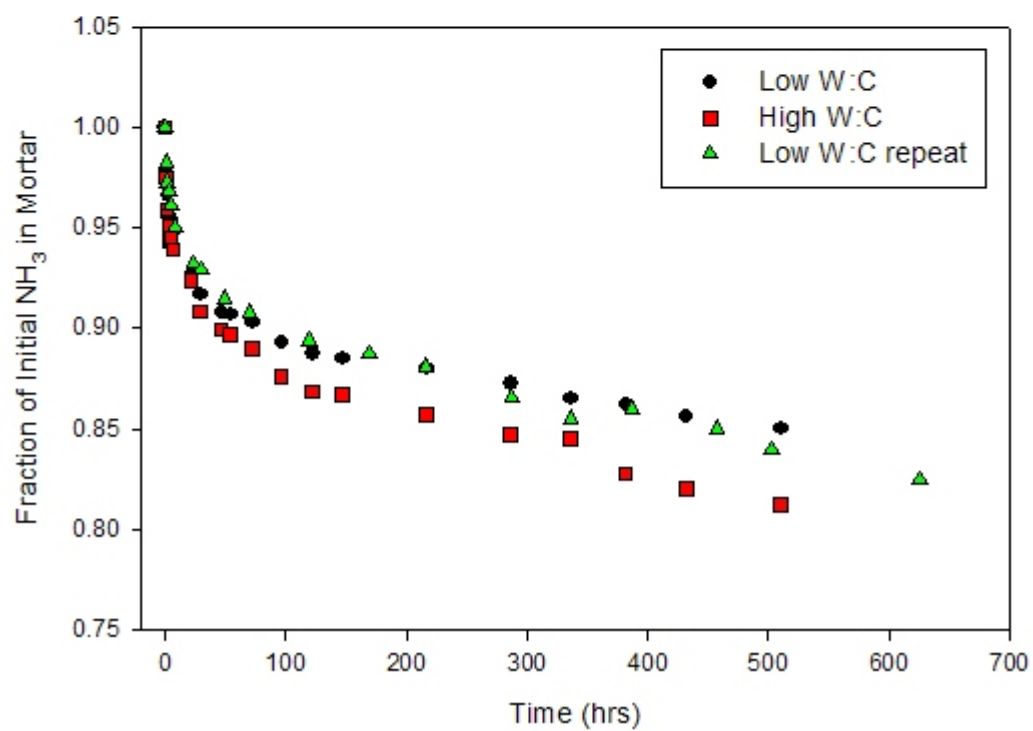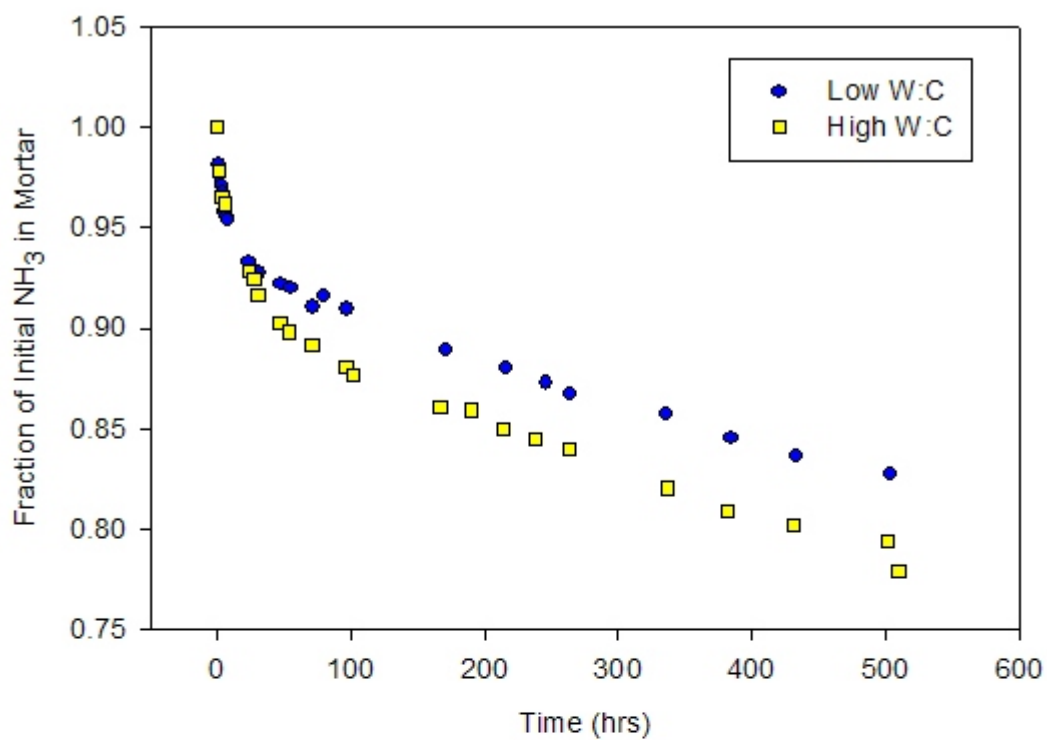
Figure 6. Ammonia loss from mortar prepared with fly ash "B" (top) and "R" (bottom).
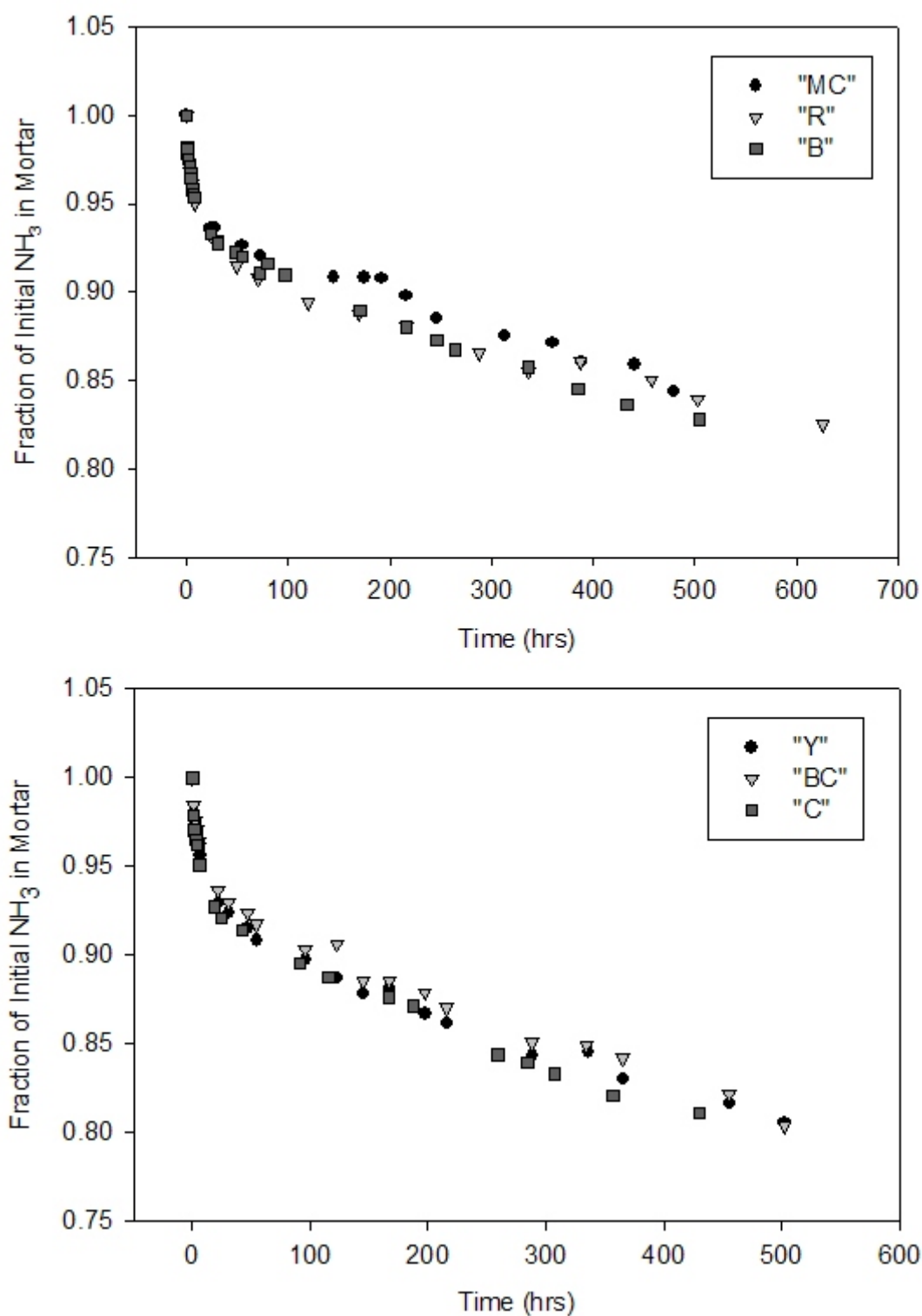
Figure 7.   Ammonia loss from mortars prepared using different non-ammoniated (top) and ammoniated (bottom) fly ashes.
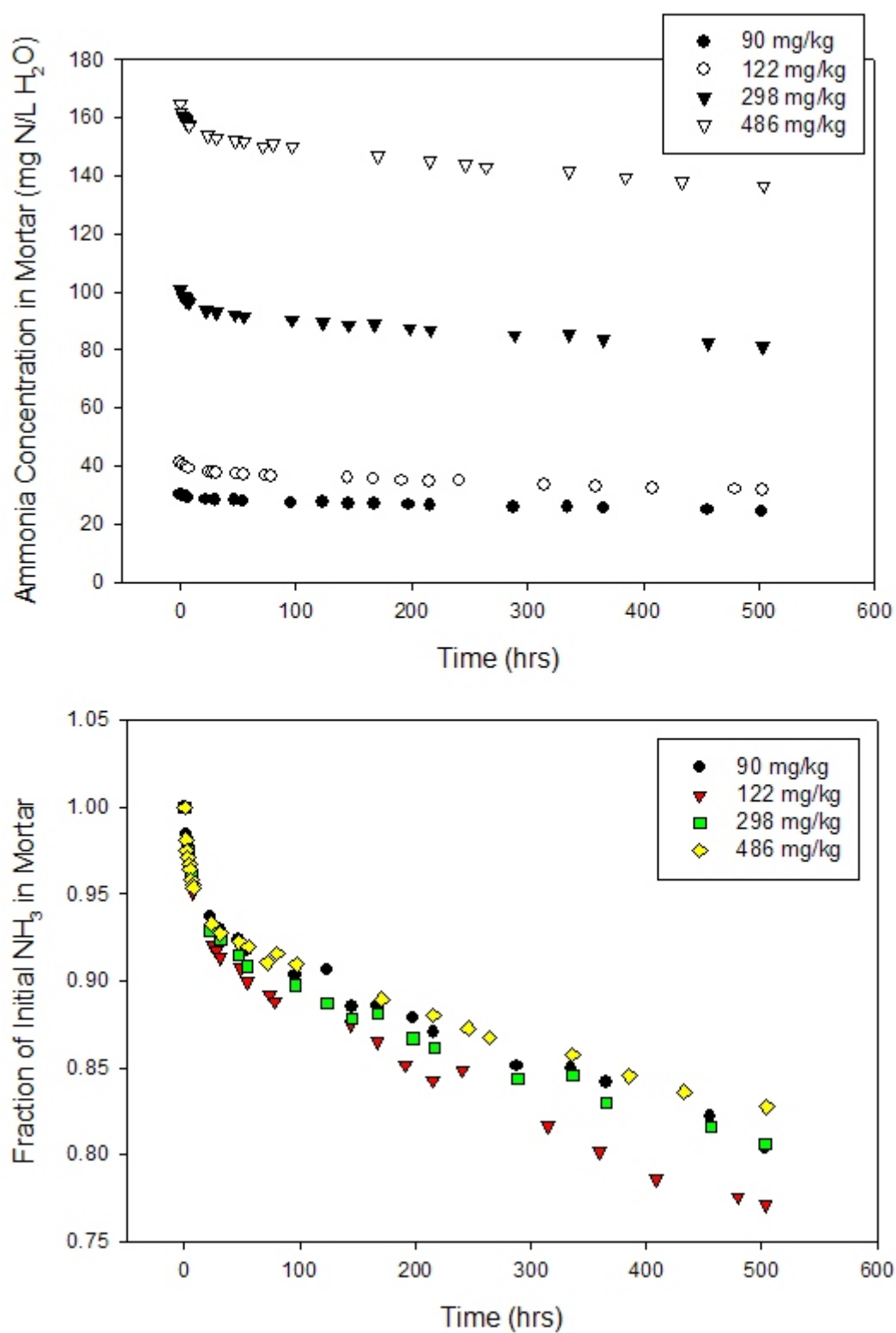
Figure 8.   Ammonia loss from mortar expressed as mg/L (top) and as a fraction of
            initial concentration (bottom). Numbers in the legend refer to NH_3
            concentration on a fly ash basis.
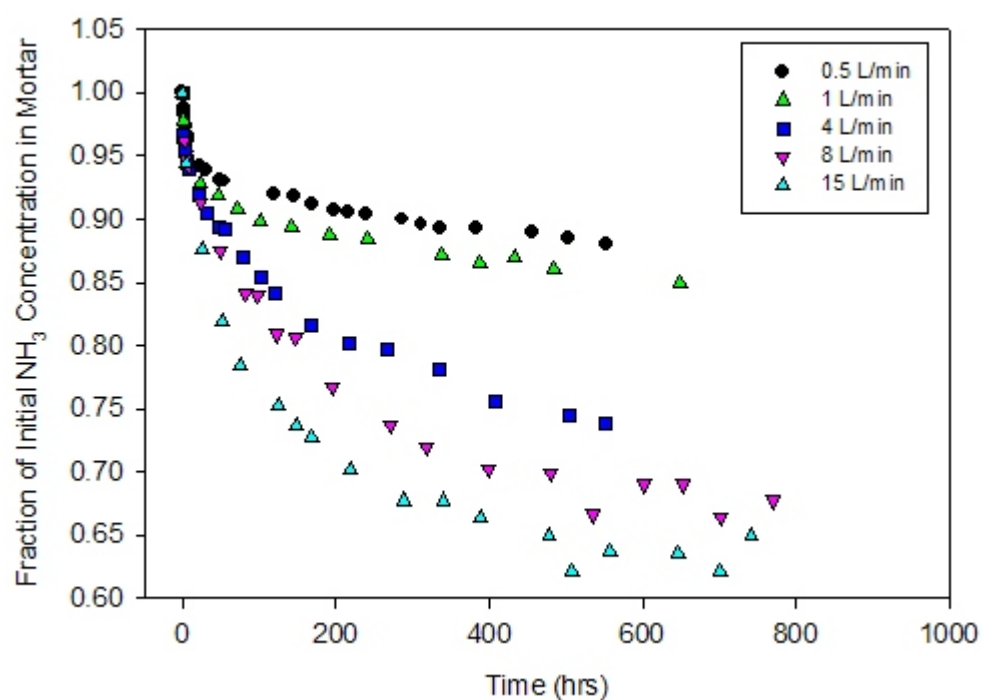
Figure 9.   The loss of ammonia from mortar as a function of ventilation rate.
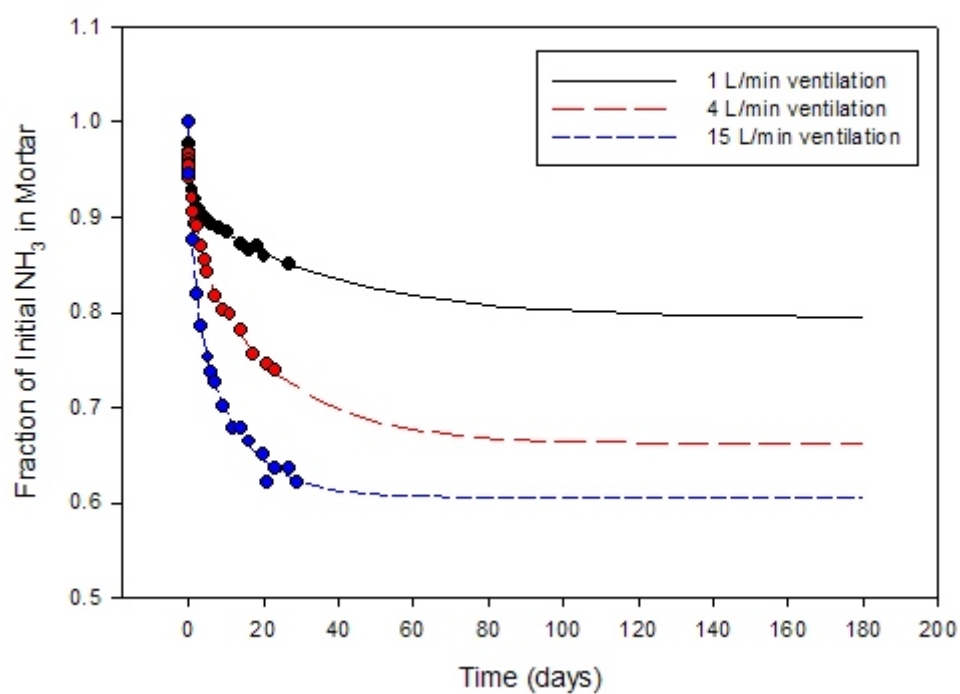
Figure 10.   Extrapolation of selected ammonia loss data shown in Figure 9.
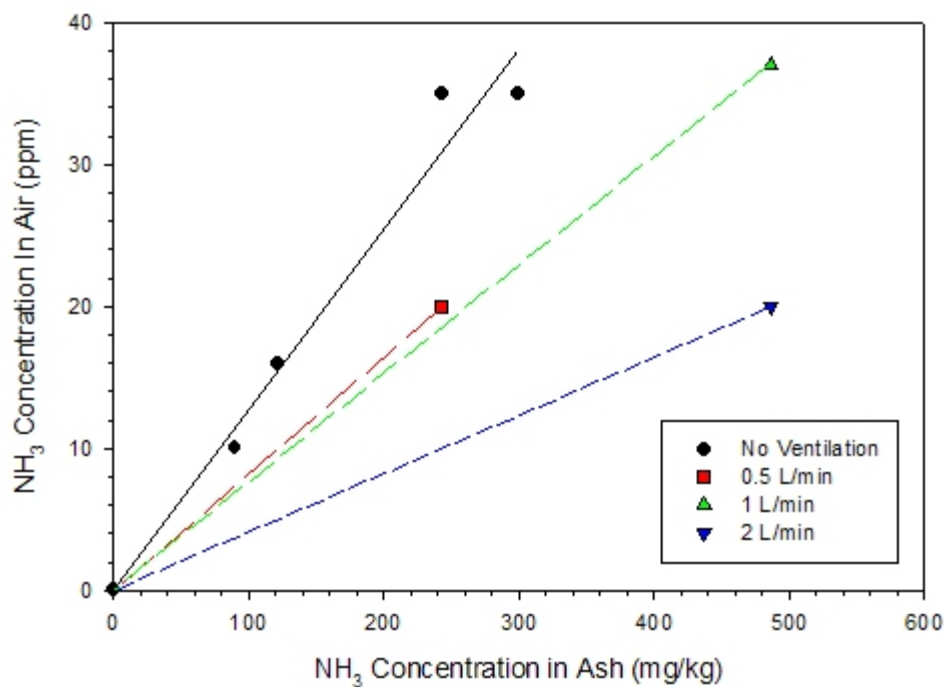
Figure 11.   The concentration of ammonia in the air above mortar, as a function of ventilation rate through the apparatus shown in Figure 2.
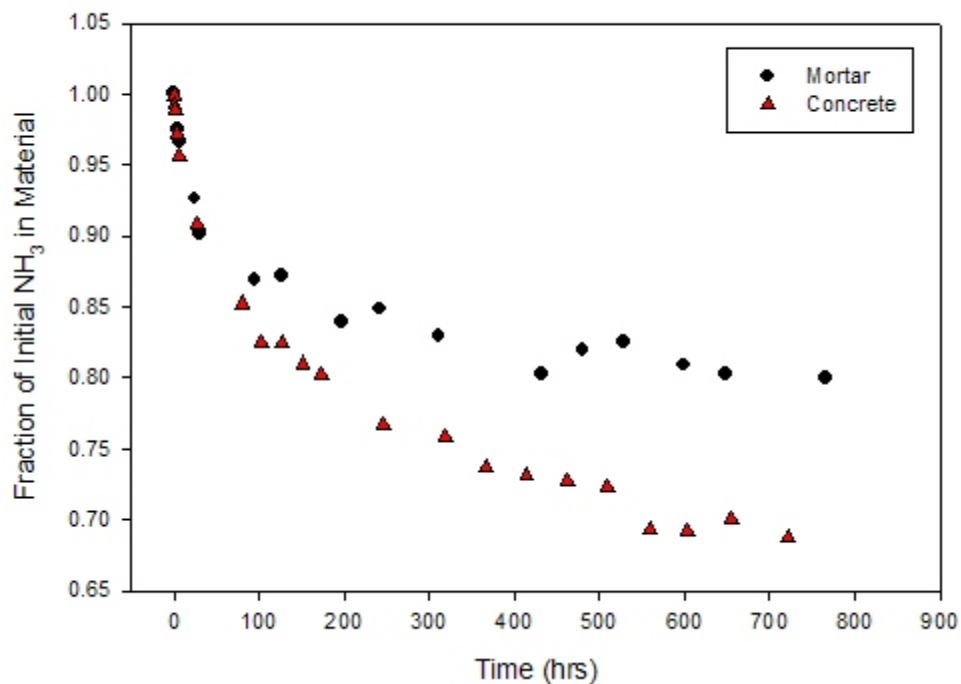
Figure 12.   Comparison of ammonia loss rate from mortar and concrete of similar thickness and equivalent ventilation rates.
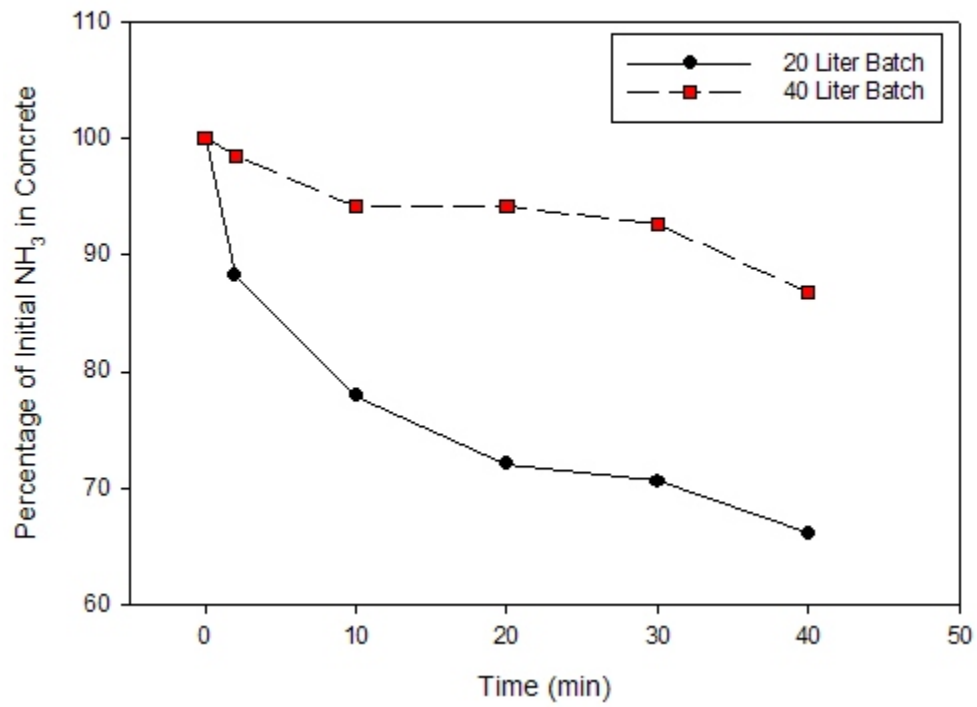
Figure 13.   The loss of ammonia from concrete during mixing of different batch sizes.
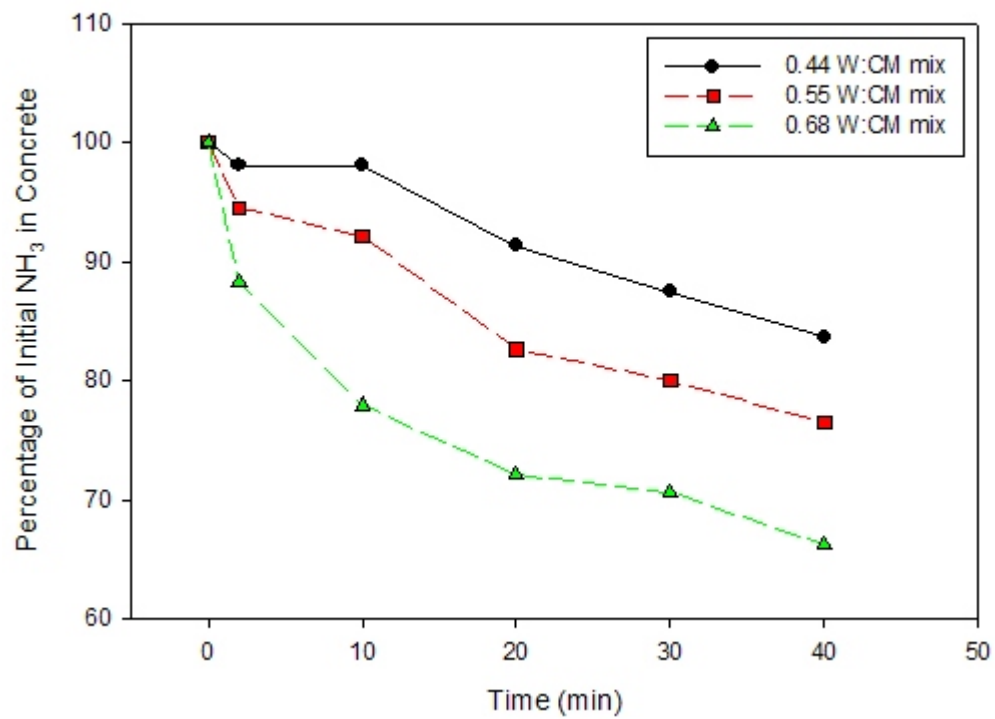
Figure 14.   The loss of ammonia during mixing of different concretes.
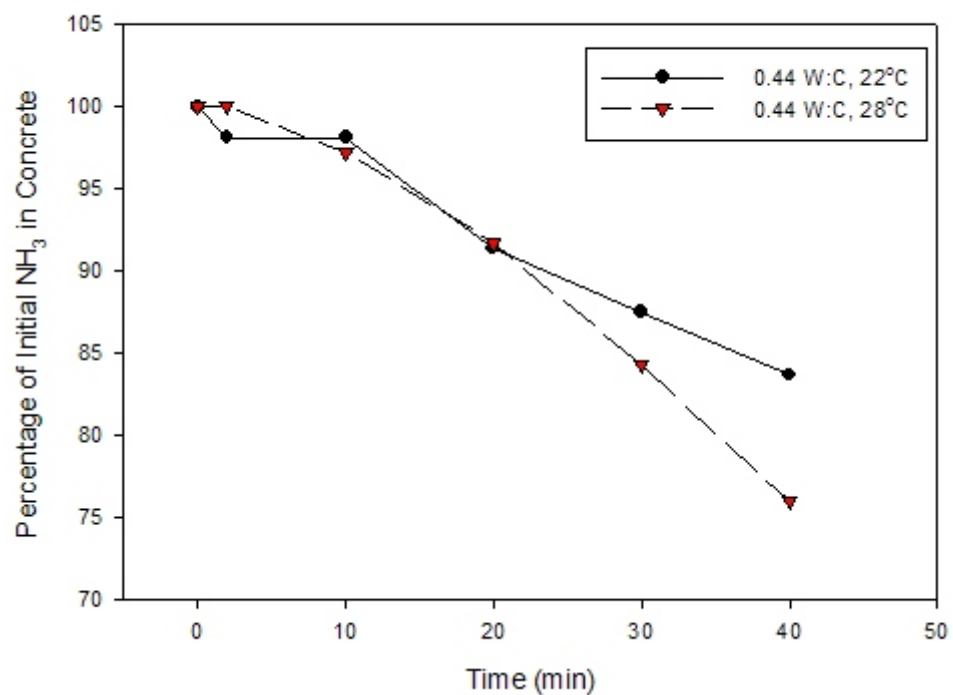
Figure 15.   The effect of temperature on ammonia loss during concrete mixing.
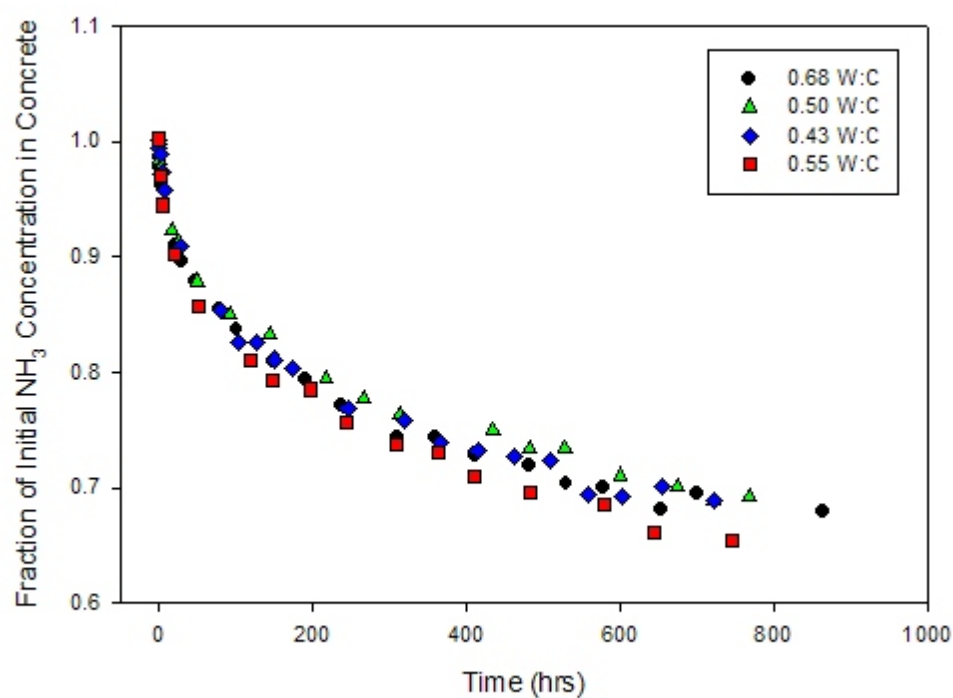
Figure 16.   Long-term ammonia loss from different concrete mixes.
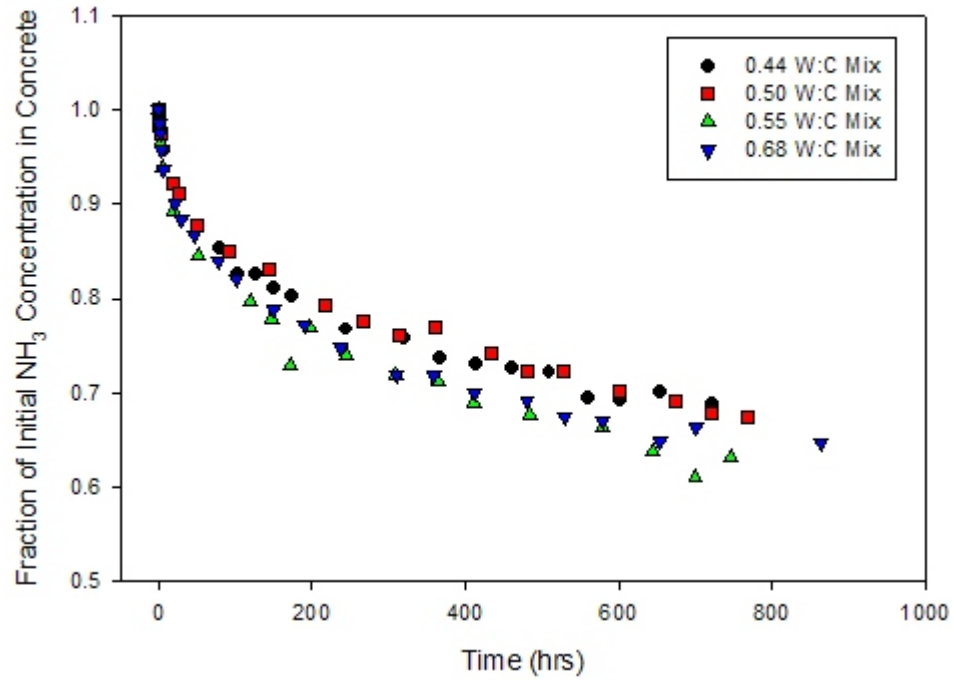
Figure 17.   "Corrected" long-term ammonia loss data.
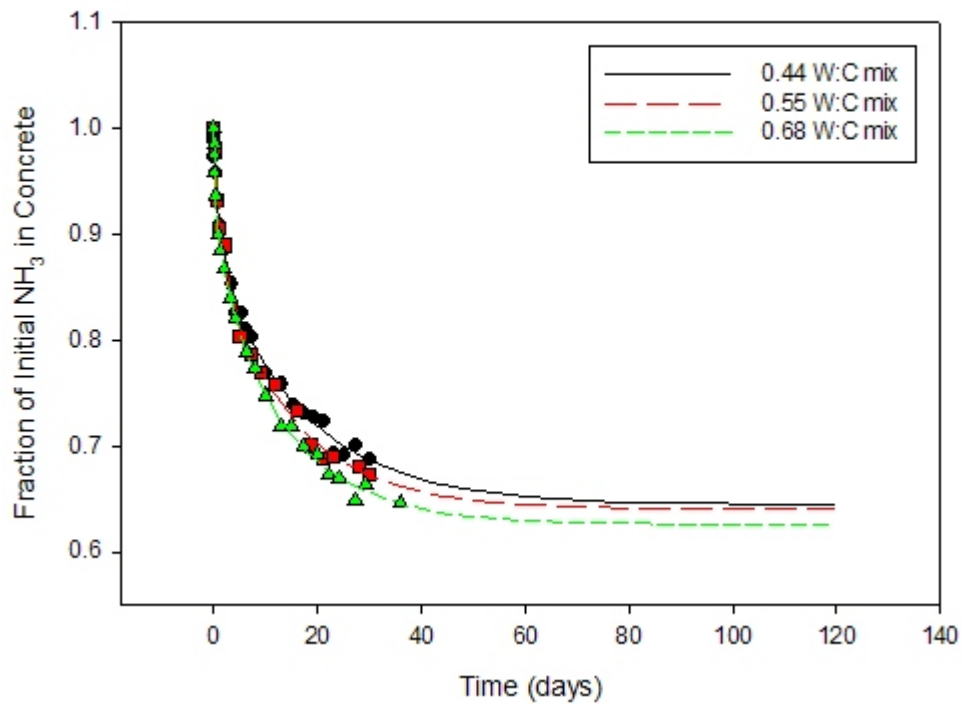
Figure 18.   Long-term ammonia loss data that have been mathematically fitted and extrapolated to four months duration.

50
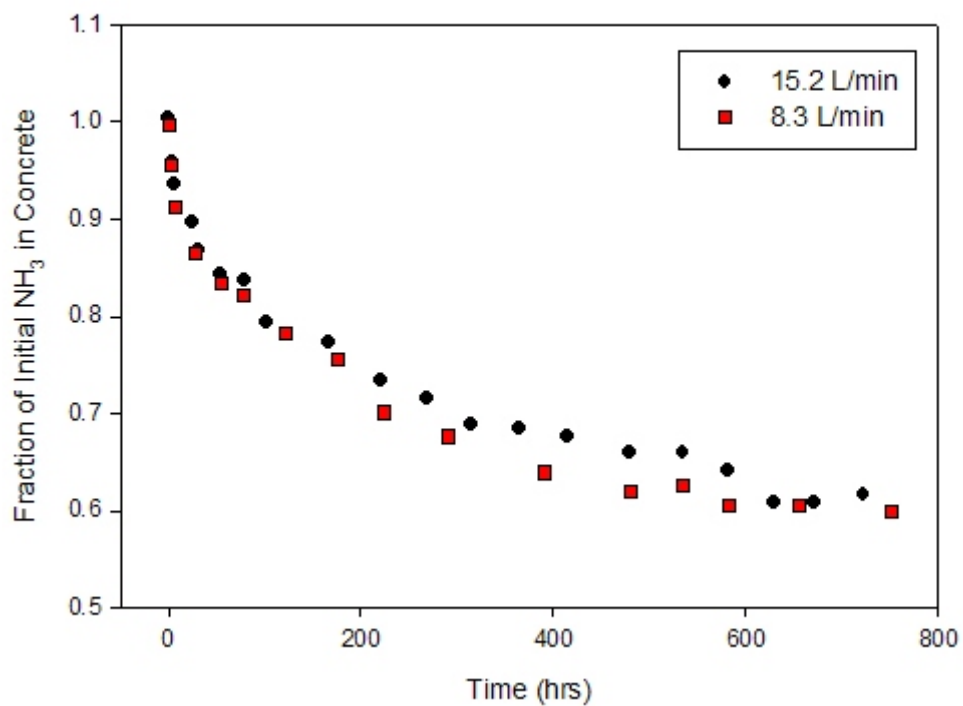
Figure 19.   Long-term ammonia loss from concrete that was exposed to two different ventilation rates.
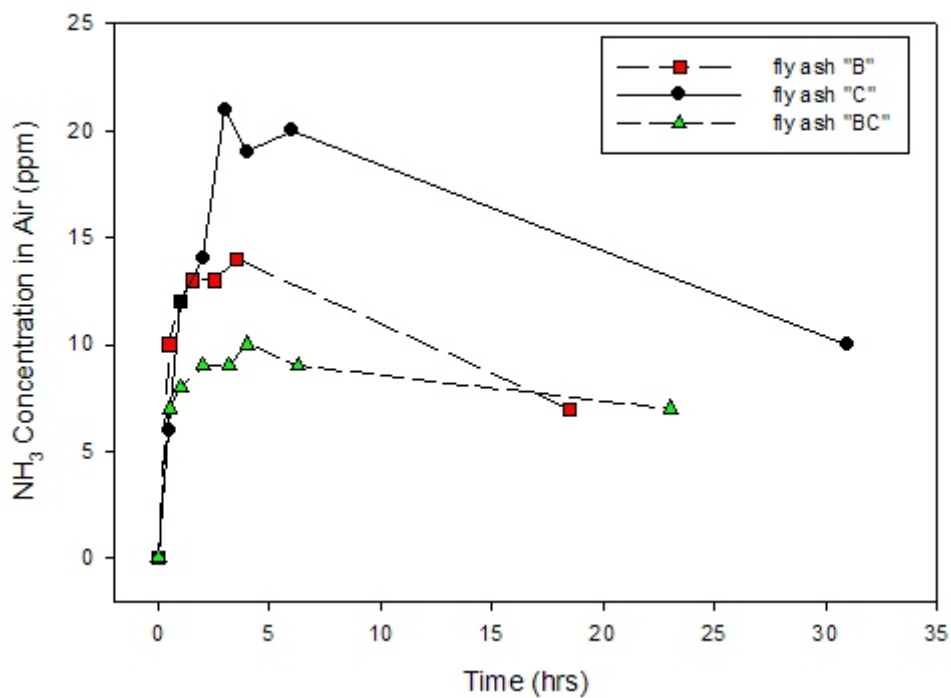
Figure 20.   Ammonia concentration in the air above concrete without ventilation.
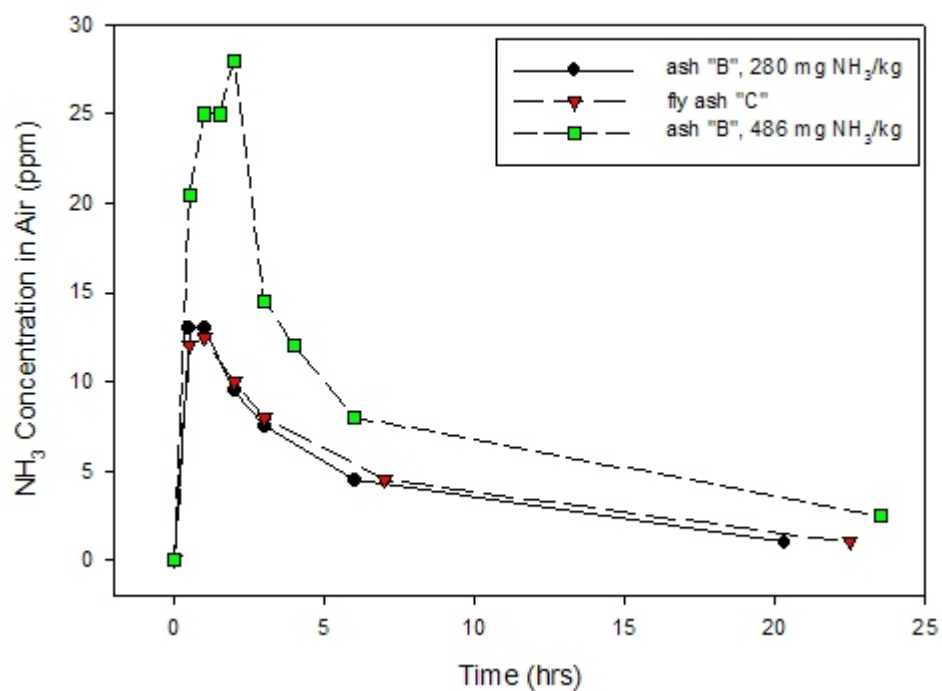
Figure 21. NH_3 concentration in the air above concrete, with 8.3 L/min ventilation.
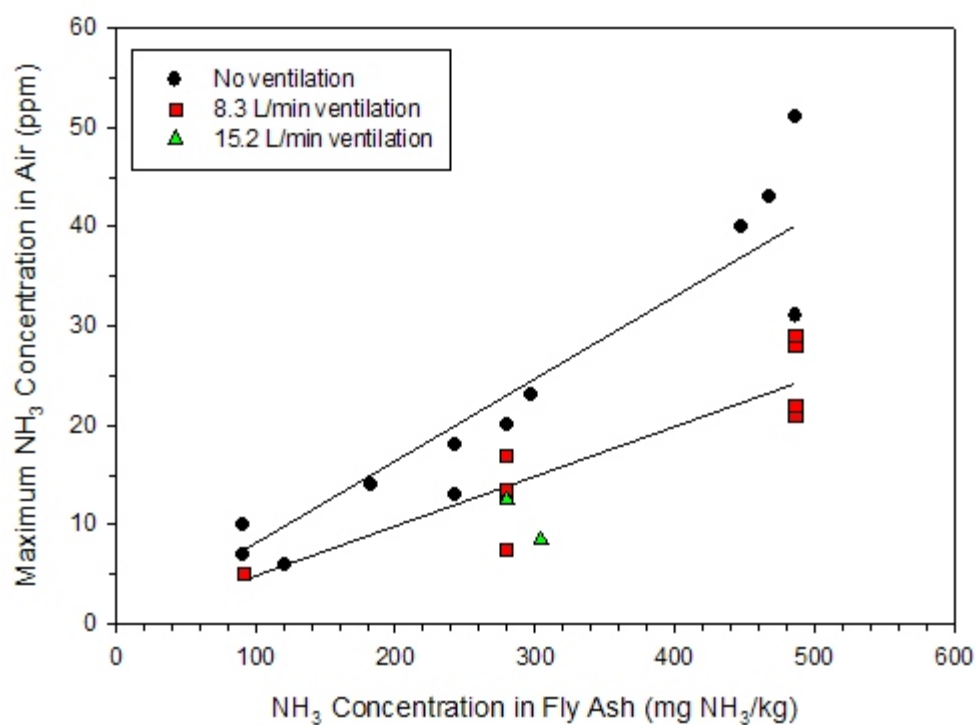
Figure 22. Maximum NH_3 concentration in the air above fresh concrete vs. NH_3 concentration in the fly ash, using different ventilation rates.
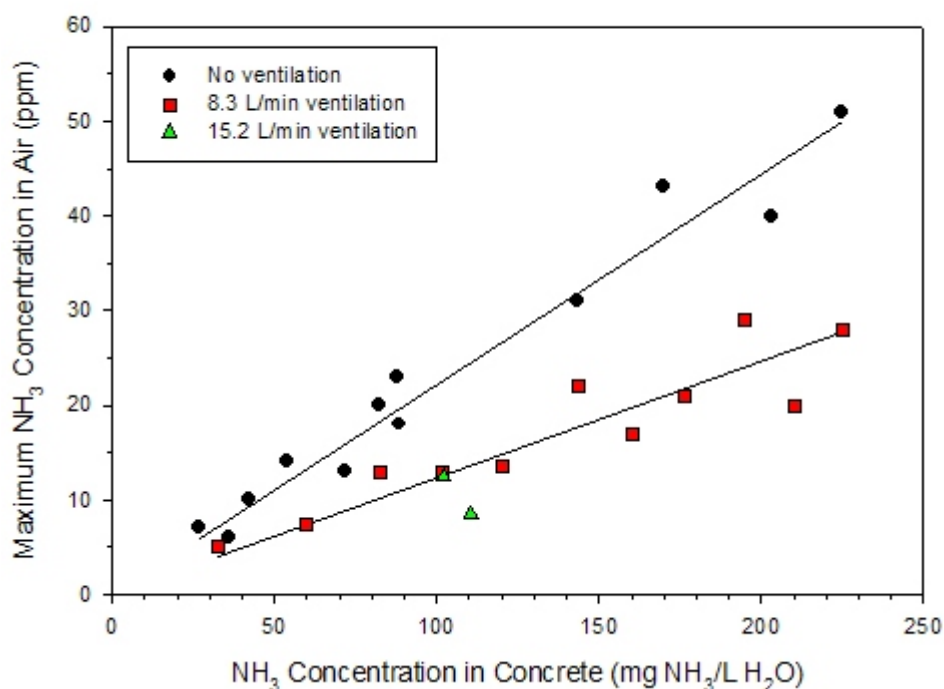
Figure 23.   Maximum NH_3 concentration in the air above fresh concrete vs. NH_3 concentration in the concrete water, using different ventilation rates.
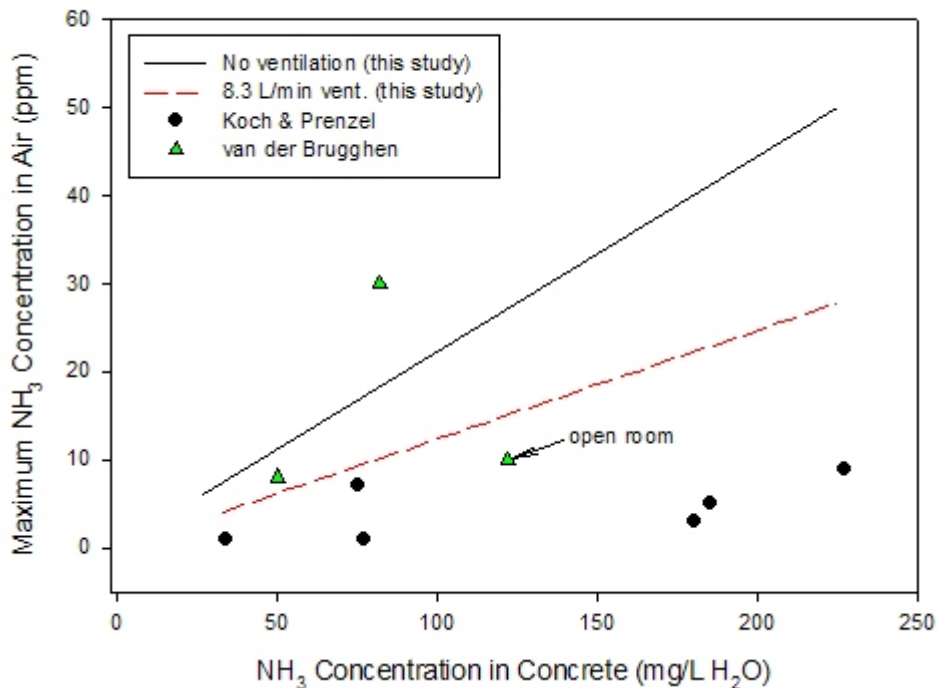

Figure 24.   Comparison of Koch and Prenzel (1989) and van der Brugghen (1995) data with results of this project.

Figure 25.   Ready Mix concrete truck used for the large-scale experiments.

Figure 26.   Finishing of test slab (Batch #1).

Figure 27.   Storage buildings used for large-scale ammonia monitoring experiments.

Figure 28.   Construction of vinyl building within concrete forms.

Figure 29.   Discharge of concrete into a building. Note plastic curtains placed over door opening during discharge.

Figure 30.   Draeger monitor and pump used to detect ammonia within the buildings.
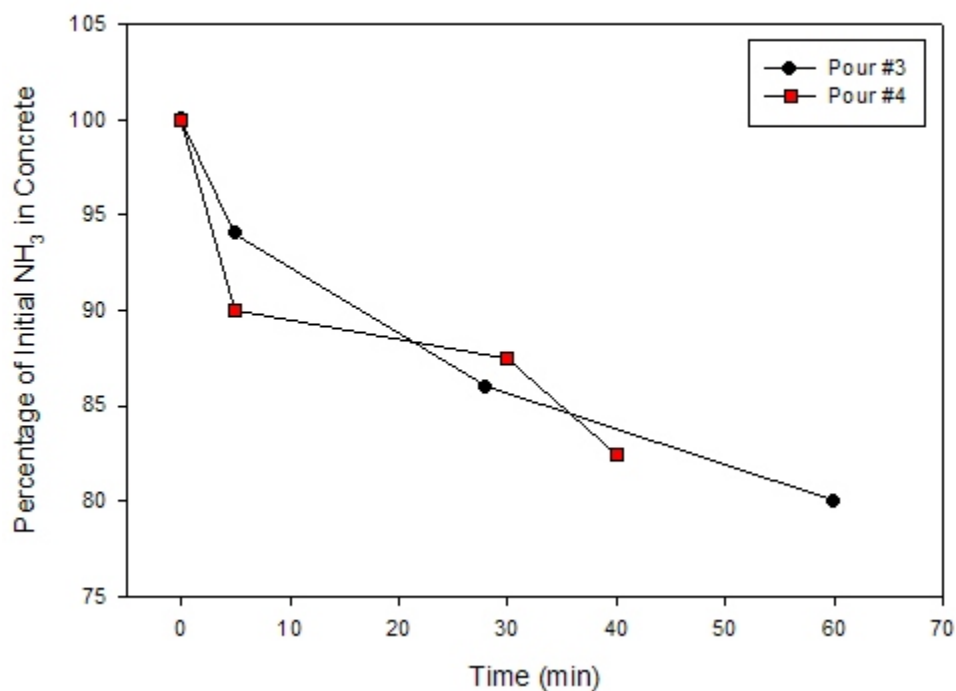
Figure 31.   Ammonia loss from concrete during mixing within the Ready Mix truck.
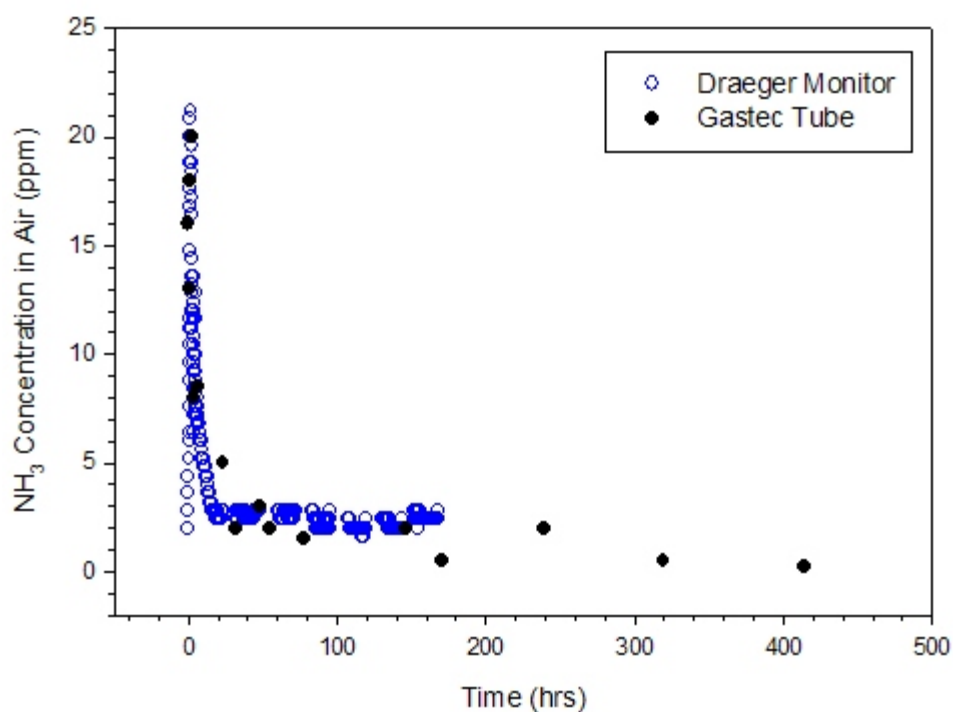

Figure 32.   The concentration of ammonia within Building #2, measured using the
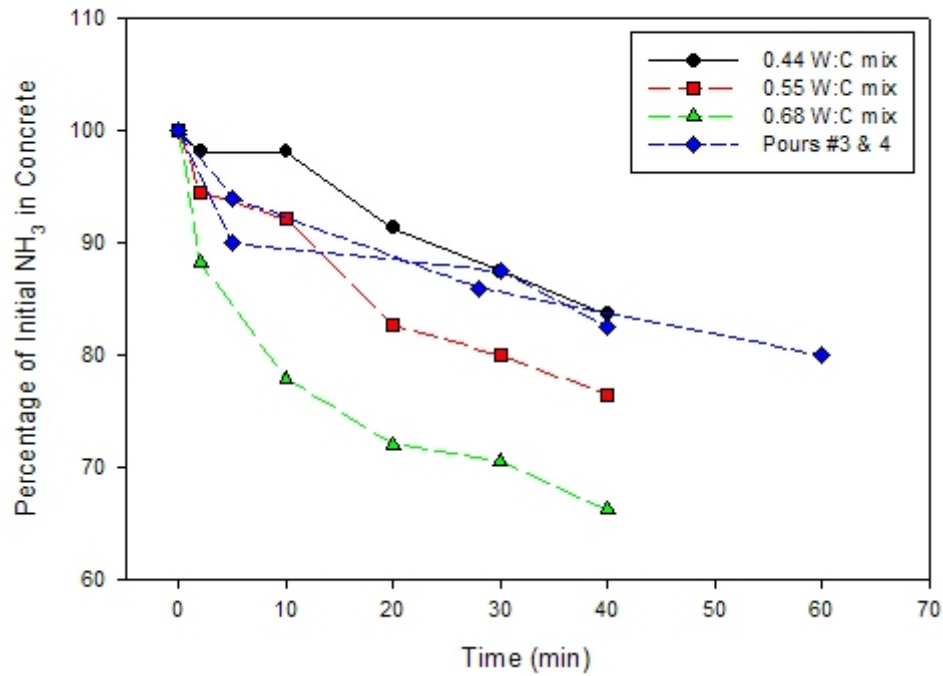Draeger monitor and GasTec tubes.

Figure 33.   The loss rate of ammonia during concrete mixing: comparison of field and laboratory data.
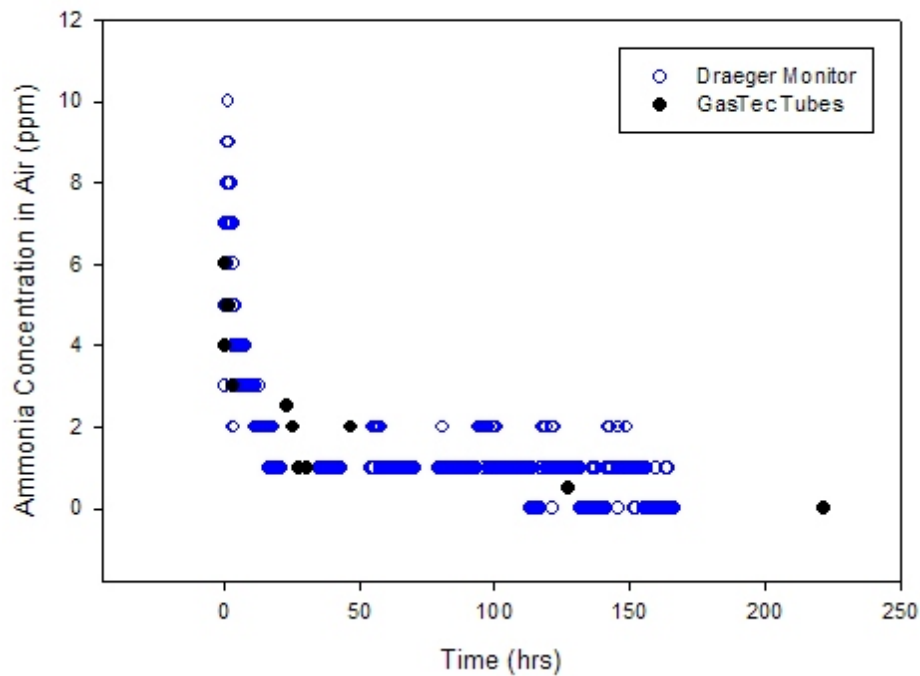

Figure 34.   The concentration of ammonia within Building #3, measured using the Draeger monitor and GasTec tubes.
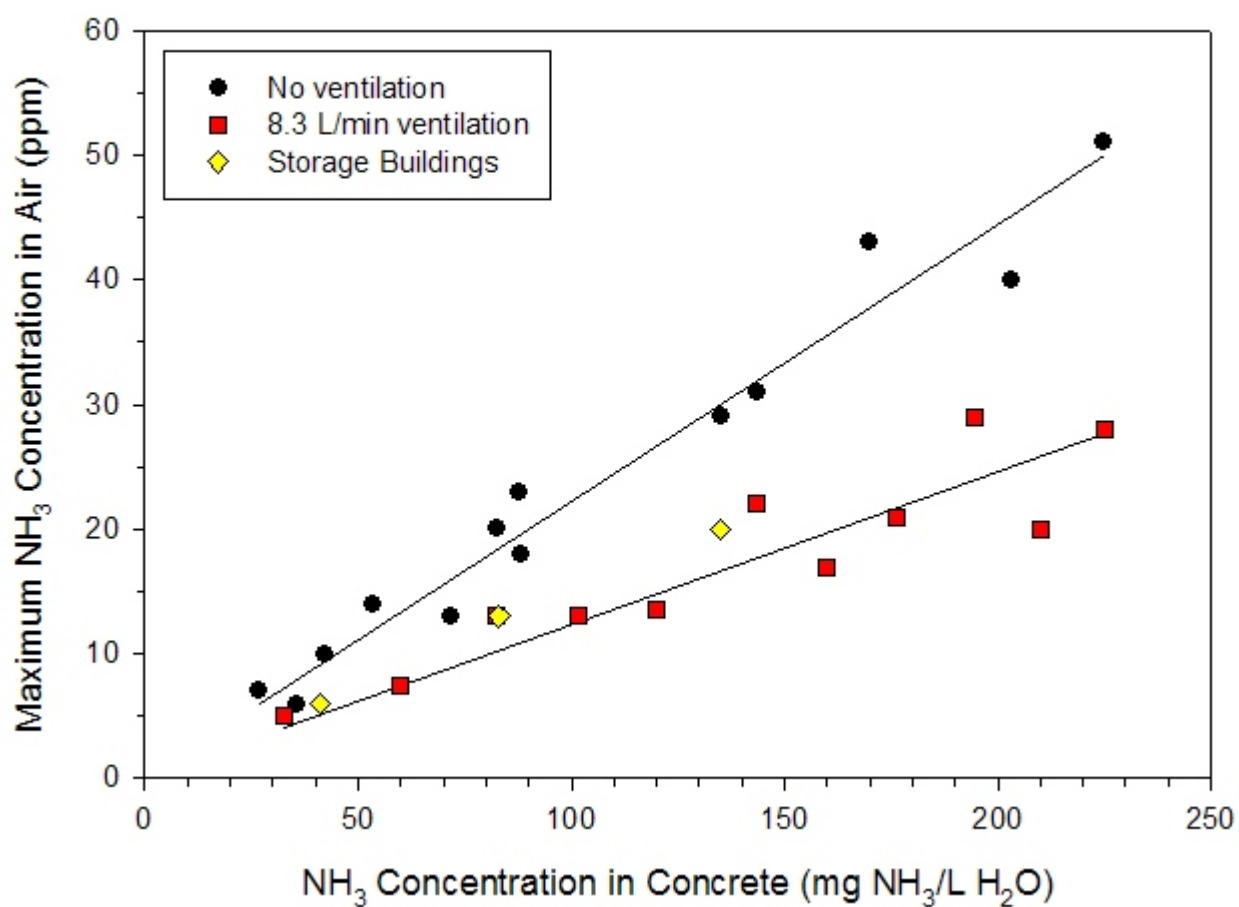
Figure 35.   Comparison of laboratory and field (i.e. storage building slab) data, on the maximum concentration of ammonia in the air above fresh concrete.

APPENDIX

Evaluation of Ammonia Measurement Techniques and Validation of Experimental Methods Used in This Study

I. Ammonia Capture in Acidic Solution

The stability of ammonium ion in the trap solution was evaluated prior to mortar testing. To accomplish this, 250 ml of a 10 mg/L ammonia (as N) trap solution was placed in a stoppered Erlenmeyer flask containing a fritted glass bubbler. A 1 L/min flow of air was passed through the solution over the course of two weeks, and the ammonium concentration periodically measured. After 14 days, the ammonium concentration, as determined using the Orion ISE, remained between 10-11 mg/L. This test also showed that the ambient air contained negligible ammonia contamination.

The accuracy of the experimental method was assessed by preparing 250ml of a 200 mg/L ammonia as N source solution (with added NaOH), and bubbling 1 L/min air through the solution. The air stream was then bubbled through 250 ml of trap solution, followed by bubbling through a second trap solution. After 24 hrs, the ammonia remaining in the "source" solution was measured using the Orion gas-sensing electrode, whilst ammonia remaining in the trap solutions was measured using the ammonium ISE. Table A1 provides a summary of the results and indicates that the technique provided an accurate measurement of ammonia lost from a basic solution, and that an insignificant quantity of ammonia escapes the first trap flask (at the 1 L/min flow rate).

Table A1. Test of Ammonium Acetate-Acetic Acid "Trap" Solution

Solution	Initial Concentration (mg N/L soln)	Final Concentration (mg N/L soln)
Source	200	10
Trap #1	0	191
Trap #2	0	<1

II. Test of Sonotube Apparatus

In order to accurately measure the loss rate of ammonia from concrete, the scaled-up version of the experimental design used for mortar was evaluated to ensure that ammonia could be efficiently trapped at the higher flow rates (nearly an order of magnitude) required to study concrete. In this test, a 1 L Erlenmeyer ("source") flask was filled with a 0.1 M aqueous NaOH solution containing 500 mg/L of ammonia as N. A 15 L/min flow of air was passed through the flask and then through an ammonia trap flask containing 3.5 L of the acetic acid trap solution. After 5 days the test was completed, and it was found that 96% of the ammonia was trapped in the acetic acid solution, with less than 1% remaining in the source flask. Given that the error of the ammonium electrode is approximately 4-5%, this level of recovery was considered acceptable.

In a related experiment, the Sonotube apparatus was evaluated for significant leakage

of ammonia out of the system. In this test, 3.46 L of water was placed into a polyethylene pan. Ammonium sulfate was added to the water to produce a concentration of 118 mg N/L water. Sodium hydroxide was also added to raise the pH to approximately 12. The apparatus was then assembled and 8.3 L/min (equivalent to 1 L/sec-m^2) flow of air was passed through the assembly for 9 days. Each day during the test, the ammonium ion concentration in the acetic acid trap flask was measured, whilst the remaining ammonia in the "source" pan was measured once at the end of the test. The two sets of data were then combined to calculate the percentage of initial ammonia that could be accounted for after the experiment was complete. Table A2 lists the results of the test and shows that 93-96% of the ammonia was accounted for as ammonium ion in the trap flask and as ammonia in the source pan. Figure A1 provides the ammonium ion data (from the trap flask) graphically.

Table A2. Ammonia Recovery from Sonotube Apparatus

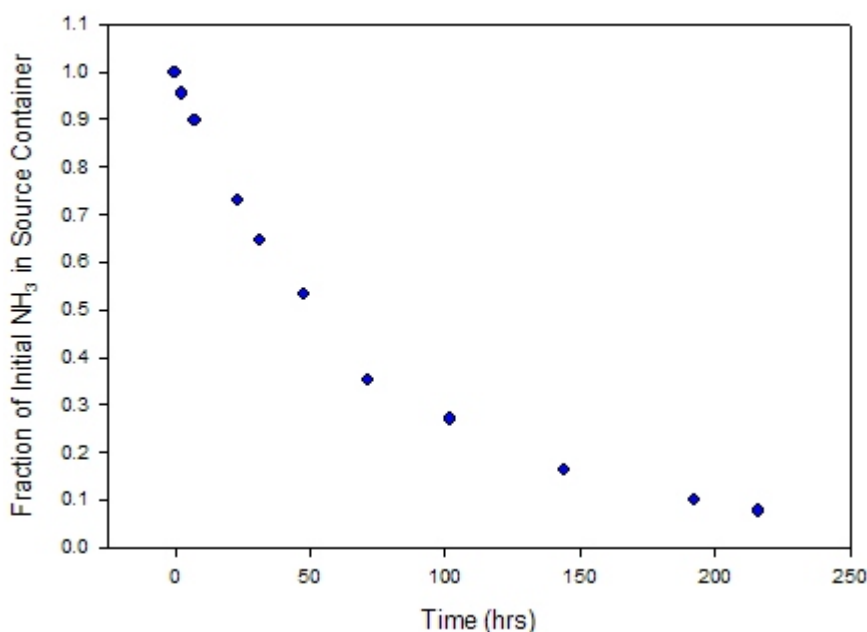|	Experiment #1		Experiment #2	
	Initial N (mg)	Final N (mg)	Initial N (mg)	Final N (mg)
Source Pan	408	6	400	32
Trap Flask	0	384	0	338
Mass Balance	96%		93%	

Figure A1. Loss of ammonia from water within the Sonotube assembly.

III. Test of Technique to Measure Ammonia in Fresh Concrete

The experimental technique was checked for accuracy by preparing cement paste, mortar, and concrete (with ammonia added to the water at 122 mg NH_3/L) within 1 L polyethylene bottles, without any external mixing. The ingredients were shaken vigorously for 10 minutes, whereupon the ammonia was measured within the bottle. Results of this testing are shown in Table A3, and indicate that the technique provided an accurate measure of ammonia in the concrete and mortar, but consistently overestimated the ammonia content for the paste. There are several possible explanations for the discrepancy. One hypothesis is that there is a greater temperature increase (from hydration) in the paste-only experiment than when aggregates are used. The higher temperature could result in a higher equilibrium concentration of ammonia in the gas phase. Another explanation is that initial hydration reactions remove water from the mixture, thus increasing the concentration of ammonia in the remaining water. However, it is not clear why this effect would not be observed in the mortar and concrete experiments. Additional work is needed to determine the cause of the discrepancy.

**Table A3. Ammonia Concentration of Fresh Concrete
Prepared in a Polyethylene Bottle**

Material	Actual NH_3 (mg/L H_2O)	Measured NH_3 (mg/L H_2O)
Paste[1]	122	134
Mortar[2]	122	120
Concrete[3]	122	120

[1] Cement, ash, water; [2] Cement, ash, sand, water; [3]Cement, ash, sand, gravel, water